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THE ACTION OF ETHYLENEDIBROMIDE ON PARA-NITROSODIALKYLANILINES. II.

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In an earlier paper on this subject[1] it was shown that when *p*-nitrosodimethylaniline and ethylene dibromide were heated together at a temperature of 80°–90°, the following reaction occurred :

$$4C_6H_4(NO)N(CH_3)_2 + C_2H_4Br_2 = [C_6H_4(NO)N(CH_3)_2]_2C_2H_2 + 2C_6H_4(NO)N(CH_3)_2HBr.$$

That is, the hydrobromide of nitrosodimethylaniline and a base, formed from the union of 2 molecules of dimethylaniline and the acetylene group, were produced. One of the structural formulas then suggested for this base was

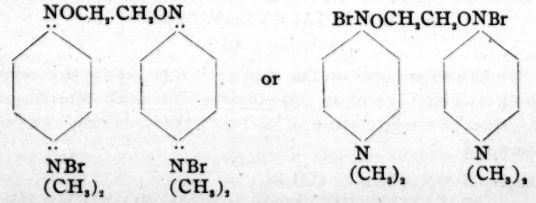
$$(CH_3)_2NC_6H_4N-CHCH-NC_6H_4N(CH_3)_2.$$

[1] THIS JOURNAL, 28, 107.

That this is actually its constitution is now proved, since it is found to be identical with the tetramethyldiaminoglyoxim-N-phenyl ether obtained by H. v. Pechmann and W. Schmitz by the action of diazomethane on *p*-nitrosodimethylaniline.[1] It was shown by these authors that the formation of glyoxim-N-phenyl ethers was a general reaction for diazomethane on aromatic nitroso compounds.[2]

In this reaction of ethylene dibromide some intermediate compound is very likely formed before the glyoxim-N-phenyl ether is produced, since the latter compound consists of 2 molecules of *p*-nitrosodimethylaniline united by

but acetylene itself does not act on *p*-nitrosodimethylaniline, whereas, with methyl iodide and benzoyl chloride it has been shown that addition-products are formed.[3] Such an intermediate body with ethylene dibromide was not isolated, but, as was suggested in a former paper, it is highly probable that an addition-product such as



is formed, which splits off hydrobromic acid with the production of the tetramethyldiaminoglyoxim-N-phenyl ether. If the reaction of ethylene dibromide on *p*-nitrosodimethylaniline is carried on in alcoholic solution, tetramethyldiaminoazoxybenzene is produced. A certain amount of this body is also formed, together with the glyoxim ether, if the temperature is allowed

[1] Ber. d. chem. Ges., **31**, 293.
[2] *Ibid*., **30**, 2461, 2871.
[3] *Ibid*., **26**, 1756; **30**, 933.

to rise too high when the two substances are heated together alone.

The melting-point given by v. Pechmann and Schmitz for the glyoxim derivative is 245°, while that given by me is 230°–240°, but decomposition occurs and the point of decomposition depends, somewhat, upon the rapidity of heating. A further proof of its identity is given by its conversion into tetramethyldiaminoglyoxaldianil, by means of dilute nitric acid, a reaction observed by v. Pechmann and Schmitz with hydrochloric acid. The glyoxim phenyl ether is very unstable toward mineral acids.

When 5 grams of this body were slowly added to 38 cc. of 15 per cent nitric acid, diluted with 38 cc. of water, a solid separated which proved to be the nitrate of *p*-nitrosodimethylaniline, as shown in a former paper.[1] When the precipitate was removed by filtration and the filtrate was made alkaline by sodium carbonate, a reddish-yellow precipitate fell, which was collected on a filter, washed with water and alcohol and dried on a clay plate. By crystallization from toluene a body was obtained in the form of yellow plates, melting at 256°–257°.

The analysis, melting-point and reaction of this compound show it to be tetramethyldiaminoglyoxaldianil,

$$(CH_3)_2NC_6H_4N : CHCH : NC_6H_4N(CH_3)_2.$$

I. 0.2003 gram substance gave 0.5391 gram CO_2 and 0.1437 gram H_2O.

II. 0.1408 gram substance gave 0.3753 gram CO_2 and 0.1016 gram H_2O.

III. 0.0902 gram substance gave 15 cc. N at 21°.3 and 765 mm.

	Calculated for $[(CH_3)_2NC_6H_4N]_2C_2H_2$.	Found. I.	II.	III.
C	73.47	73.41	72.70	. .
H	7.48	7.97	8.02	. .
N	19.04	. .	. .	19.26

Properties of Tetramethyldiaminoglyoxaldianil.—As would be expected, reduction of this body by zinc and sulphuric acid

[1] THIS JOURNAL, 28, 107.

gives *p*-aminodimethylaniline, which was isolated by adding an excess of sodic hydrate and shaking out with ether. The ethereal solution, dried with solid potassic hydrate, gave, after distilling off the ether and evaporating in a dry vacuum, colorless crystals which, on crystallization from ligroin, melted at 37°–39° (m. p. *p*-aminodimethylaniline 41°). These crystals gave a strong methylene blue reaction.

That the glyoxalanil is itself somewhat hydrolyzed by dilute acids is evident from the fact that such solutions give the methylene blue reaction.

The weakness of the union at the double bonds is still further illustrated by the products obtained by the action of salicylic aldehyde and benzoyl chloride.

Action of Salicylic Aldehyde on Tetramethyldiaminoglyoxaldianil.

When the dianil is boiled with an alcoholic solution of salicylic aldehyde it is converted, almost quantitatively, into *o*-oxybenzylidene-*p*-aminodimethylphenylamine :

$$(CH_3)_2NC_6H_4N:CHCH:NC_6H_4N(CH_3)_2 + 2HOC_6H_4CHO = 2(CH_3)_2NC_6H_4N:CHC_6H_4OH + OCHCHO.$$

Five grams of the dianil were boiled for 40 minutes with 1 gram of salicylic aldehyde, dissolved in 45 cc. of alcohol. From this, filtered hot, there separated, on cooling, beautiful orange plates which melted at 134°–135°. The melting-point was not raised by recrystallization.

The melting-point, the analytical results which are given below and a comparison with a sample of *o*-oxybenzylidene-*p*-aminodimethylphenylamine, made directly from *p*-aminodimethylaniline and salicylic aldehyde,[1] leave no doubt as to its identity. Analysis :

I. 0.2480 gram substance gave 0.6791 gram CO_2 and 0.1520 gram H_2O.

II. 0.1701 gram substance gave 18.35 cc. N at 26°.5 and 764 mm.

[1] Ber. d. chem. Ges., 18, 593.

	Calculated for $(CH_3)_2NCH_4N:CHC_6H_4OH$.	Found. I.	II.
C	75.00	74.66	. .
H	6.66	6.81	. .
N	11.66	. .	12.01

Action of Benzoyl Chloride on Tetramethyldiaminoglyoxaldianil.—By repeated treatment of the dianil with benzoyl chloride and dilute sodic hydrate, a cleavage of the molecules occurs and benzoyl *p*-aminodimethylaniline is formed.

When the benzoyl chloride is first added the dianil is taken up by the acid chloride, with formation of a dark-green mixture. After repeated treatment and frequent stirring, a light-colored product was obtained. The aqueous, alkaline solution was poured off, the residue was treated with alcohol, collected on a filter, dried on a clay plate and crystallized from boiling benzene, it separated in the form of silk-like needles. The product melted at 223°–224° and recrystallization failed to raise the melting-point. This is somewhat lower than that given by Börnstein (228°), who prepared the compound by the direct action of benzoyl chloride on *p*-aminodimethylaniline. The analytical results are those required for monobenzoyl *p*-aminodimethylaniline.[1]

I. 0.1485 gram substance gave 0.4040 gram CO_2 and 0.0911 gram H_2O.

II. 0.1449 gram substance gave 15.6 cc. N at 24° and 758 mm.

	Calculated for $(CH_3)_2NC_6H_4NHCOC_6H_5$.	Found. I.	II.
C	75.00	74.20	. .
H	6.66	6.82	. .
N	11.66	. .	12.05

Although tetramethyldiaminoglyoxaldianil is hydrolyzed by mineral acids, it gives a bronze-colored salt when chloroform solutions of the dianil and picric acid are mixed. With alcoholic mercuric chloride it gives a blue precipitate. It also gives a blue color with extremely dilute chloroform or benzene solutions of bromine, chlorine, hydrochloric acid and acid chlorides.

[1] Ber. d. chem. Ges., 29, 1482.

Chloroform, when perfectly pure, dissolves it with a yellow color, but when this solvent has begun to decompose even very slightly, the color produced is green or blue.

Action of Ethylene Dibromide on p-Nitrosodiethylaniline.[1]

Tetraethyldiaminoglyoxim-N-phenyl Ether.—When *p*-nitrosodiethylaniline and ethylene dibromide were heated together on the steam-bath the reaction became so violent that it was uncontrollable, but it proceeded smoothly enough if the two substances, in the proportions of 1 part of the base to 4 parts of the ethylene dibromide, were allowed to stand at the ordinary temperature for a day or two. After the interval, a dark-colored solid separated, which was collected on a filter and dried on a porous plate. The products of this reaction are tetraethyldiaminoglyoxim-N-phenyl ether and the hydrobromide of *p*-nitrosodiethylaniline, which were isolated in the following manner: The hydrobromide was decomposed and dissolved out from the glyoxim derivative by treatment with alcohol and dilute sodic hydrate. After thoroughly washing with alcohol and drying, the product was crystallized several times from amyl alcohol. Addition of absolute ethyl alcohol to the amyl alcohol solution aided in the crystallization. The body decomposed at about 207°, the temperature depending somewhat on the rapidity of heating. That this body is identical with the tetraethyldiaminoglyoxim-N-phenyl ether obtained by v. Pechmann and Schmitz by the action of diazomethane is shown by its melting-point, its properties and the analytical results given below:

I. 0.1196 gram substance gave 0.2996 gram CO_2 and 0.0840 gram H_2O.

II. 0.1518 gram substance gave 0.3814 gram CO_2 and 0.1108 gram H_2O.

III. 0.2266 gram substance gave 27.2 cc. moist N at 22° and 764 mm.

[1] This reaction was studied some time ago with Mr. A. L. Kelley at the University of Vermont.

	Calculated for $[(C_2H_5)_3NC_6H_4N]_2C_2H_2O_4$.	Found. I.	II.	III.
C	69.11	68.32	68.52	. .
H	7.85	7.80	8.11	. .
N	14.66	. .	. .	14.67

I wish to express to Mr. W. W. Farnum my indebtedness to him for his assistance in certain portions of this work.

THE CONDUCTIVITY AND VISCOSITY OF SOLUTIONS OF CERTAIN SALTS IN MIXTURES OF ACETONE WITH METHYL ALCOHOL, WITH ETHYL ALCOHOL AND WATER.

By Harry C. Jones and Eugene C. Bingham.

PART I.

HISTORICAL REVIEW.

(*a*) *Conductivity and Viscosity.*—That viscosity and conductivity are related is by no means a new idea. As early as 1856, G. Wiedemann[1] studied aqueous solutions of copper sulphate and concluded that the conductivity of a solution is directly proportional to the concentration and inversely proportional to the viscosity. When formulated this would be:

$$\frac{K\eta}{p} = \text{constant},$$

where K is the conductivity of the solution of concentration, p and η the viscosity.

Grotrian,[2] in 1876, measured the conductivity and viscosity of solutions at different temperatures, but obtained indecisive results.

Stephan,[3] in 1883, tried a third possibility, by using mixtures of alcohol and water as a solvent. He found the temperature coefficients of conductivity and of fluidity (the reciprocal of viscosity) very much alike. He observed a minimum in his curves and proposed the formula:

[1] Pogg. Ann., 99, 229 (1856).
[2] *Ibid.*, 157, 130 (1876).
[3] Wied. Ann., 17, 673 (1883).

$$\frac{KH}{k\eta} = \text{constant},$$

to hold up to the minimum point, and

$$\frac{wKH}{w'k\eta} = \text{constant}$$

to hold from that point on; where K is the conductivity of the equivalent aqueous solution, k the conductivity of the mixture and H and η, the corresponding viscosities. w and w' are the per cents of water in the given aqueous mixture and in the aqueous alcoholic mixture of minimal fluidity, respectively. He believed that each ion carries with it neighboring molecules of the solvent, and that ionic friction results from the friction between these and the rest of the solvent.

Dutoit and Friderich[1] introduced the association factor and concluded that, "The values of μ_v for a given electrolyte dissolved in different solvents, are a direct function of the degree of polymerization of the solvent and an indirect function of the coefficient of viscosity of these solvents."

A fourth method of changing the fluidity was resorted to by Röntgen,[2] and later by Warburg and Sach,[3] and more exhaustively by Cohen.[4] They subjected the aqueous solution to high pressure. Cohen found that, at low temperatures, the viscosity is decreased by the pressure, but that above 40° the viscosity increases with the pressure. In concentrated solutions of sodium and ammonium chlorides the viscosity increases nearly proportionally to the pressure and nearly independently of the temperature. Hauser[5] showed that, at 32°, the pressure ceased to affect the fluidity of water.

Grossman,[6] in 1883, recalculated Grotrian's results and found that the conductivity multiplied by the viscosity gave a constant independent of the temperature, and that the temperature coefficients were the same to within 1 per cent.

[1] Bull. Soc. Chim., [3], **19**, 321 (1898).
[2] Wied. Ann., **22**, 510 (1884).
[3] *Ibid.*, **22**, 514 (1884).
[4] *Ibid.*, **43**, 666 (1892).
[5] Ann. d. Physik., **5**, 597 (1901).
[6] Wied. Ann., **18**, 119 (1883).

Arrhenius[1] worked with aqueous solutions, to which small amounts of non-electrolytes, such as acetone and methyl and ethyl alcohols, had been added. He pointed out an empirical relation between the conductivity and the fluidity, but he saw that these quantities are not simply dependent on each other, because the conductivities of dilute solutions of different salts are not the same. This empirical relation was further developed by Euler.[2]

We need only mention the work of Stringberg[3] and of Holland.[4]

Völlmer[5] investigated solutions of various salts in methyl and ethyl alcohols. He found the temperature coefficients of conductivity and fluidity to be very nearly identical.

Kohlrausch and Deguisne[6] used a formula,

$$K_t = K_{18}[1 + \alpha\,(t - 18°) + \beta(t - 18°)^2],$$

to represent the influence of temperature on conductivity, starting from 18° as a mean temperature. Kohlrausch[7] noted that on extrapolating this curve, aqueous solutions would reach a zero value of conductivity at about —39°, which is about the temperature where the fluidity would become zero. Bousfield and Lowry[8] showed that the viscosity of water may be represented accurately by a formula similar to the above,

$$\eta_{18} = \eta_t\,[1 + \alpha(t - 18) + \beta(t - 18)^2].$$

They found that the constants α and β are the same in the two formulas, to within the limits of experimental error. They believe, however, that these formulas will not hold at low temperatures and that the zero values cannot be experimentally realized. This belief is borne out by the work of Kunz.[9]

In an exceedingly interesting paper, Kohlrausch[10] proposes the view that "About every ion there moves an atmosphere of

[1] Z. physik. Chem., **9**, 487; *Ibid.*, **1**, 285 (1887).
[2] *Ibid.*, **35**, 536 (1898).
[3] *Ibid.*, **14**, 221 (1894).
[4] Wied. Ann., **50**, 261 (1892).
[5] *Ibid.*, **52**, 328 (1894).
[6] Dissertation, Strassburg, 1893.
[7] Sitz. Berlin., (1901), 1028.
[8] P. Roy. Soc., **71**, 42 (1902).
[9] Compt. rend., **135**, 788 (1902).
[10] P. Roy. Soc., **71**, 338 (1903).

the solvent, whose dimensions are determined by the individual characteristics of the ion. . . . . The electrolytic resistance is a frictional resistance that increases with the dimensions of the atmosphere. The direct action between the ion and the outer portion of the solvent diminishes as the atmosphere becomes of greater thickness. . . . . For a very sluggish ion there will be only the friction of water against water, and the electrolytic resistance will have the same temperature coefficient as the viscosity of water, provided the atmosphere itself does not change its dimensions with the temperature. If, however, the atmosphere becomes, for example, smaller with increasing temperature, the temperature gradient of the conductivity might be greater than that of the fluidity. According to observations now at hand, this would seem to be the case for the slowest moving univalent ion, Li."

Bousfield and Lowry[1] have gone farther and have shown that we should also expect to find an upper limit of conductivity, on account of the decrease in dissociation with rise in temperature. A maximum conductivity of this sort has been observed by Franklin and Kraus[2] in liquid ammonia. Potassium iodide gives a maximum in conductivity, in methyl alcohol, at 160°.[3] Noyes[4] observed a maximum conductivity with 0.1 N potassium and sodium chlorides, in water, at 280°. The formula of Slotte[5] for variation of fluidity,

$$\eta_0/\eta = (1 + bt)^n,$$

holds at low temperatures, so that combining this formula with that of Abegg and Seitz for decrease in dielectric constant,

$$D/D' = e^{-at},$$

Bousfield and Lowry[6] give, as the complete formula representing the effect of temperature on conductivity,

[1] *Loc. cit.*
[2] THIS JOURNAL, 24, 83 (1900).
[3] Physic. Rev., 18, 40 (1904).
[4] Z. physik. Chem., 46, 323 (1903). J. Am. Chem. Soc., 26; 134 (1903).
[5] Beibl., 16, 182 (1892).
[6] P. Roy. Soc., 74, 280 (1904).

$$\frac{K_t}{K_0} = \frac{\rho_v}{\rho_0}(1 + bt)^n e^{-at}.$$

Reference should also be made to the work of Hechler.[1]

(*b*) *Viscosity.*—The majority of workers have confined themselves either to viscosity determinations alone, or to conductivity determinations alone. We must, therefore, consider some of these if we wish to see clearly the relations between the phenomena.

We need simply mention here the work of Poiseuille,[2] Noack,[3] Pagliani and Battelli,[4] Slotte,[5] Gartenmeister[6] and Traube.[7] The monumental work of Thorpe and Rodger[8] requires more attention. They worked with very great accuracy both with pure liquids[9] and with mixtures,[9] and over a considerable range of temperature. They have shown that the formula of Slotte gives the best results. They proved, conclusively, what had been hinted at before, that "Viscosity may be taken as the sum of the attractive forces in play between the molecules; . . . . . that an increment of CH_2 in chemical composition, or the substitution of an atom of Cl, Br, or I for an atom of hydrogen, brings about a definite change in the magnitude of the viscosity. It is, therefore, made evident that viscosity or intermolecular attraction is, in reality, a property of the atoms of which the molecules are composed. Isomers have nearly, but not the same viscosity, yet the effect of CH_2 is the same as in the normal compounds. The effects due to ring grouping, iso- and double-linkages, and changes in the condition of the oxygen may be quantitatively allowed for. . . . . But water and the alcohols show no agreement with the calculated values."

Hydrogen is calculated to have an effect on molecular viscosity of 44.5, carbon of 31 and iso-linkage, for example, of

[1] Dissertation, Münster (1904).
[2] Mem. Inst. Paris, **9**, 433 (1846).
[3] Wied. Ann., **27**, 289 (1886).
[4] Atti. di R. Ac. delle Sc. d. Torino, **20**, 607 (1885).
[5] *Loc. cit.*
[6] Z. physik. Chem., **6**, 524 (1890).
[7] Ber. d. chem. Ges., **19**, 871 (1886).
[8] Phil. Trans., **185A**, 307 (1894).
[9] J. Chem. Soc., **51**, 360 (1897).

—21. The effect is shown in the following table, giving the "molecular viscosity at slope 0.0000323."

Table I.

	Normal compound.		Iso-compound.	
	Found.	Calculated.	Found.	Calculated.
Pentane	687	689	663	668
Hexane	818	809	799	788
Heptane	931	929	908	908
Octane	1035	1049		

They found both maxima and minima when working with mixtures and, in the particular case of chloroform and ether, they found a point of inflection. They believe that the maximum value is caused by a "feeble chemical combination or molecular aggregation, which is destroyed by heat or dilution."

It is to be expected that water and the alcohols would give abnormal results, since Ramsay and Shields[1] have shown that these liquids are associated. They are also abnormal in possessing a high dielectric constant.[2] Some of the characteristic properties of water, methyl alcohol, ethyl alcohol and acetone are grouped together below:

Table II.

	Mol. vol.	Viscosity.	Association.	Dielectric constant.
Water	18.0 at 0°	0.01778 at 0°	1.707 at 0°	79.46 at 0°
	18.1 at 25°	0.00891 at 25°	1.644 at 20°	73.92 at 20°
Methyl alcohol	39.5 at 0°	0.0080846 at 0°	2.65 at −90°	34.05
	40.3 at 20°	0.005530 at 25°	2.32 at 20°	
Ethyl alcohol	57.1 at 0°	0.017761 at 0°	2.03 at −90°	25.02
	58.3 at 20°	0.0108545 at 25°	1.65 at 20°	
Acetone	70.9 at 0°	0.0039496 at 0°	1.26 at 17°–78°	21.85
	73.2 at 20°	0.0030726 at 25°		

[1] Z. physik. Chem., **12**, 433 (1893); **15**, 111 (1894).
[2] *Ibid.*, **14**, 286 (1894).

No such quantitative relation has been worked out for changes in viscosity caused by salts brought into solution, and still less is known about the conductivity which a given salt may be expected to give. Yet Bredig,[1] Wagner[2] and Euler[3] have worked on this problem with considerable success. Wagner found that the viscosity of a salt solution is an additive function of the metallic and non-metallic radicals of the dissolved salt. For allied metals the viscosity decreases as the atomic weight increases. The dissociated ions appear in some cases to have greater, and in other cases less viscosity than the original solution.

To explain this "negative viscosity" shown by certain salts in their power to lower the viscosity of pure water, Euler employed the "Electrostriction theory" proposed by Drude and Nernst.[4] According to this theory the ion is surrounded by a strong electrical field, in virtue of its charge, which causes a strong compression of the liquid in this field. Euler holds that the effect of a salt on viscosity is the result of two tendencies; first, that of the atoms tending to increase the viscosity in inverse proportion to their migration velocities and, second, the electrostriction tending to lessen the viscosity.

Euler has calculated viscosity constants for a large number of ions and finds the relation between them and the migration velocities to be expressed by the formula

$$(A - 0.68).U (\text{or } (K - 0.68).V) = \text{a constant},$$

where A and K are the viscosity constants and U and V are the migration velocities of the anion and cation, respectively. Hydrogen and hydroxyl ions are exceptions. Some of the values given are the following:

Table III.

Ion.	Migration velocity.	Viscosity constant.
Li	39.8	1.15
Ca	62.0	1.023
K	70.6	0.962
Br	73.0	0.946
NO_3	..	0.919

[1] Z. physik. Chem., **13**, 243 (1894).
[2] *Ibid.*, **5**, 31 (1890).
[3] *Ibid.*, **25**, 536 (1898).
[4] *Ibid.*, **15**, 79 (1894).

Wagner[1] has shown that Mullenbein's[2] measurements have discounted Euler's explanation of negative viscosity, since the viscosity of the solvent may be lowered by the addition of certain non-electrolytes, even when the viscosity of the dissolved substance is higher than that of the solvent. With ethyl alcohol, *o*-nitrotoluene gives an inversion-point, *m*-nitrotoluene a minimum and *p*-nitrotoluene a maximum.

He proposes, as an explanation, that the solute diminishes the quantity of the solvent in a given space and this leads to a diminution of the viscosity, which diminution is partly compensated, however, by the solute itself. According to the relative magnitude of the various factors, the viscosity may be increased or diminished.

Dunstan[3] has investigated a large number of mixtures. He believes that the increase in viscosity is due to the formation of loosely-held complexes. He thinks that the cause of the minimum of viscosity is more deep-seated than Wagner supposed and attributes it to "some change in molecular aggregation or dissociation."

Blanchard[4] found that the addition of 1 equivalent of ammonia for 1 equivalent of silver, and the addition of 4 equivalents of ammonia for 1 equivalent of copper and zinc in aqueous solutions of their salts, very greatly decreases the viscosity. He reasons that this cannot be due to increased ionization, and therefore rejects the electrostriction theory and proposes a hydrate theory. He says that if the positive ion consists solely of a metallic atom bearing an electric charge, combination with ammonia molecules cannot decrease its mass or readily increase its symmetry, so as to reduce the viscosity. The only explanation seems to be that the ions in solution are hydrated. The hydrate water is replaced by ammonia, which forms with the ion a more stable complex and one of smaller mass, or greater symmetry, or both. He believes that this theory also accounts for negative viscosity and for the effect of pressure on viscosity. Evidently, this is the same conclusion as that

[1] Z. physik. Chem., 46, 867 (1903).
[2] Dissertation, Leipzig, 1901.
[3] J. Chem. Soc., 85, 817 (1904). Z. physik. Chem., 49, 590 (1904).
[4] J. Am. Chem. Soc., 26, 1315 (1904).

reached by Kohlrausch in his hypothesis of ionic spheres, but by a somewhat different method of approach.

Blanchard added small amounts of water to alcoholic solutions of sodium hydroxide and found the viscosity smaller than would be expected from a study of the pure solvents. This is due, as he thinks, to the formation of a complex between the alkali, water and alcohol, which is, however, smaller or more symmetrical than the alcohol-water complex originally present.

Mixtures of alcohol and water give a maximum of viscosity. Blanchard finds that cupric chloride increases this effect. He further applies this theory to the work of Jones and Lindsay,[1] on conductivity.

The existence of hydrates or solvates (in the case of non-aqueous solvents) in one form or another is an old conception. Poisseuille[2] first suggested it in working with alcohol and water. Graham[3] confirmed and extended Poisseuille's work. Wijkander[4] supposed that acetic acid forms a hydrate with water, $C_2H_4O_2.H_2O$, which would account for abnormal viscosity. The changes due to temperature he attributed to dissociation changes in the liquid. Thorpe and Rodger[5] and Traube[5] also assume the presence of hydrates.

Recently, Varenne and Godefroy[6] have found evidence from viscosity curves for the existence of various hydrates in mixtures of water with methyl and ethyl alcohols and acetone. These are as follows:

Table IV.

Methyl alcohol and water.	Ethyl alcohol and water.	Acetone and water.
$CH_3OH.H_2O$	$C_2H_5OH.2H_2O$	$CH_3COCH_3.3H_2O$
$CH_3OH.2H_2O$	$C_2H_5OH.3H_2O$	$CH_3COCH_3.4H_2O$
$CH_3OH.3H_2O$	$C_2H_5OH.6H_2O$	$CH_3COCH_3.8H_2O$
$CH_3OH.5H_2O$	$3(C_2H_5OH).2H_2O$	$CH_3COCH_3.34H_2O$
$CH_3OH.8H_2O$	$C_2H_5OH.22H_2O$	
$CH_3OH.20H_2O$		

[1] THIS JOURNAL, 28, 329 (1902).
[2] *Loc. cit.*
[3] Phil. Trans., 151, 373 (1861).
[4] Weid. Beibl., 8, 3 (1879).
[5] *Loc. cit.*
[6] Compt. rend., 137, 992 (1903): 138, 990 (1904).

This conception of the existence of hydrates differs from the view put forward by Jones,[1] according to which the composition of the hydrates is simply a function of the concentration, the temperature remaining constant. The composition may vary all the way from 1 molecule of water to a large number, every intermediate step being represented. Various lines of evidence have been furnished for this view by Jones,[2] Jones and Getman,[3] and Jones and Bassett.[4] The more important of these have to do with the relation between water of crystallization and lowering of the freezing-point, certain color changes in solution and the relation between water of crystallization and temperature.

(*c*) *Conductivity.*—A great number of researches have been made on conductivity, using a large number of electrolytes and many different solvents. It is necessary to take up only that work which will help to bring out the relation between conductivity and viscosity.

In general, solvents that show abnormal conductivities when electrolytes are dissolved in them, have abnormal viscosities. Dutoit and Aston[5] advanced the idea that dissociating power is related to the amount of polymerization of the solvent, as determined by the surface-tension method of Ramsay and Shields.[6] On the other hand, Euler[7] has shown that potassium iodide and various other salts give considerable conductivity in nitrobenzene and other non-associated or monomolecular solvents, while in butyric and valeric acids, which are highly associated, the conductivity is very small.

The facts as found by Euler support the hypothesis proposed by Thompson[8] and Nernst,[9] which attributes the dissociating power to the high dielectric constant of the medium;

[1] THIS JOURNAL, **23**, 89 (1900).
[2] *Ibid.*, **23**, 89 (1900).
[3] Z. physik. Chem., **46**, 244 (1903). THIS JOURNAL, **31**, 303 (1904). Z. physik. Chem., **49**, 385 (1904).
[4] THIS JOURNAL, **33**, 584 (1905).
[5] Compt. rend., **128**, 240 (1897).
[6] Z. physik. Chem., **12**, 433 (1893); **15**, 111 (1894).
[7] *Ibid.*, **28**, 619.
[8] Phil. Mag., **36**, 320 (1893).
[9] Z. physik. Chem., **13**, 531 (1894).

but Eversheim,[1] and Walden and Centnerzwer[2] have shown that, although liquid sulphur dioxide has a small dielectric constant, it gives a high conductivity. Therefore, both of these relations hold only approximately.

Plotnikow[3] has shown that the dissociation is dependent somewhat upon the character of the dissolved substance, as well as upon the solvent. He obtained an abnormally great conductivity with the complex compound $AlBr_3CS_2$ in bromine solution, while most salts give little or none. He also obtained a maximum in molecular conductivity with PBr_5 dissolved in bromine, when the composition of the liquid corresponded to the formula PBr_{25}.

Zelinsky and Krapiwin[4] first noted a minimum in conductivity on mixing the solvents methyl alcohol and water. Cohen[5] noted a minimum in dilute solutions of potassium iodide dissolved in mixtures of ethyl alcohol and water. Cohen remarked that either the dissociation in all the mixtures is the same or conductivity is not a measure of dissociation.

Jones and Lindsay[6] worked with binary mixtures of methyl and ethyl alcohols and water. These alcohols and water gave a minimum at low temperatures, in most cases, and a 50 per cent mixture of methyl and ethyl alcohols gave a conductivity less than the mean value for the unmixed solvents. They proposed to account for this by assuming that each of the two associated solvents diminished the association of the other.

Jones and Carroll[7] investigated the conductivity of sodium iodide, cadmium iodide, calcium nitrate and hydrochloric acid, in mixtures of methyl and ethyl alcohols and water. The minimum was observed in all cases at low temperatures. Recalling the hypotheses of Wiedemann, and of Dutoit and Friderich, connecting viscosity and conductivity, they proposed the quantitative relation

[1] Ann. der Phys., 8, 539 (1902).
[2] Z. physik. Chem., 39, 514 (1902).
[3] *Ibid.*, 48, 220 (1905).
[4] *Ibid.*, 21, 35 (1896).
[5] *Ibid.*, 28, 31 (1898).
[6] *Loc. cit.*
[7] THIS JOURNAL, 33, 521 (1904).

$$\frac{\mu_v \eta}{x} = \text{constant} \quad \text{or} \quad \frac{\mu_v \eta}{\alpha} = \text{constant},$$

where x is the association factor and α the dissociation. These formulas become $\mu_v \eta = \text{constant}$ when $\mu_v = \mu\infty$.

This work has been continued and the relations between the viscosities and conductivities of lithium nitrate, potassium iodide and calcium nitrate, in various mixtures of acetone with methyl alcohol, ethyl alcohol and water have been worked out.

The work of Naumann,[1] on the solubility of salts in acetone, should also be mentioned.

(*d*). *Summary.*—An attempt will be made to sum up, in a brief paragraph, the factors that are already known to influence conductivity.

First, conductivity is dependent upon the number and velocity of the ions and only upon these factors, if we except the small conductivity of salts *per se*. The number of ions present is dependent upon the association factor or upon the dielectric constant of the solvent, and also upon the tendency of the atoms (or groups of atoms) to take up an electric charge, *i. e.*, more or less electro-positive or electro-negative.

The number of ions decreases with rise in temperature and with decreasing concentration. The velocity of the ions is dependent upon the fluidity of the solvent and upon the migration velocity of the ion itself. The fluidity of the solvent is, again, due to its association, to the concentration of the components having constitutive differences, and to the temperature. Pressure also affects the velocity of the ions.

Rise in temperature may decrease the association, or merely drive the molecules farther apart, giving a looser structure. The mobility of the ion is dependent upon its constitution and its affinity for the solvent, tending to produce an atmosphere of greater or less dimensions about itself.

We have not taken into account the result of the attractions between the charges on the ions, but it is not clear that the effect is measurable, and there is some doubt as to whether it is even in the direction indicated by Euler's hypothesis.

[1] Ber. d. chem. Ges., 37, 4328 (1904).

PART II.

EXPERIMENTAL.

Apparatus.

(*a*) *Conductivity.*—The Kohlrausch method of measuring conductivity, with Wheatstone bridge, telephone receiver and induction coil, was employed. It was not difficult to read to less than 0.1 of 1 per cent. The bridge wire was made of "manganin" and was calibrated before beginning the work. The resistance coils were standardized and found accurate to 0.04 of 1 per cent.

In order to work successfully with acetone, it was necessary to provide cells of special construction, so as to avoid the presence of rubber or wax,[1] which would be dissolved by the solutions. The cells were made of hard glass with ground-glass stoppers and had the form shown in Fig. I. The glass tubes

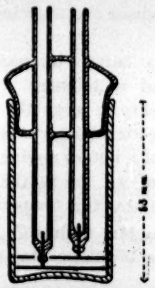


Fig. I.

carrying the electrodes were sealed into both the upper and the lower walls of the glass stopper. The distance between the electrodes thus remained permanently fixed.

The zero-bath was prepared by filling a large battery jar with clean, finely crushed ice, moistened with water. This was placed in a pail, made of compressed paper pulp and the annular space filled with finely crushed ice. Thus protected,

[1] Jones and Lindsay: *Loc. cit.*

the bath could be used for a much longer time than with the methods usually employed. The 25° bath was of the usual form, the stirrer being driven by means of a hot-air engine. An Ostwald regulator was employed. The thermometers were regulated to tenths of a degree. They were tested at the beginning of the work. Burettes and flasks were carefully calibrated.

(*b*) *Viscosity.*—The viscometer was of the form recommended by Ostwald.[1] A fixed volume of the liquid to be measured was introduced into the apparatus. The liquid was raised exactly to the mark above the bulb, by air-pressure. The air was dried with sulphuric acid. The pressure was released by means of a Mohr pinch-cock, on a thick-walled rubber tube. By this arrangement the readings agreed to within 0.2 of a second. It was important that the liquids should be given time to drain out of the tube above the upper mark, since, otherwise, a drop of liquid might collect in the upper capillary and impede the entering air, thus introducing large error.

For the zero-bath a battery jar was filled with very finely crushed ice moistened with water. The ice was renewed as often as was necessary to keep the temperature constant. For the 25° bath a 5-liter beaker was employed. The bath was stirred by means of a hot-air engine, the temperature being kept to within 0°.1 of 25°, as in the conductivity method. The room was kept as near this temperature as possible.

We are indebted to Mr. Arthur C. Macy, jeweler, for the loan of a very accurate Waltham stop-watch, reading to two-tenths of a second.

To measure the specific gravities at zero, which was necessary in order to calculate the viscosities, we constructed a pycnometer, Fig. II. (p. 495), which would allow the large expansion of the alcohols and acetone and avoid loss by evaporation.

Preparation of Solutions.

In making up mixtures of solvents, *n* cc. of acetone diluted to 100 cc. was designated as a mixture of "*n* per cent ace-

[1] Physiko-chemische Messungen, 2d Ed., p. 260.

tone." Since acetone, especially, has a high coefficient of expansion, it was important to have the temperature always the same, 20°. The acetone or alcohol was brought to this tem-

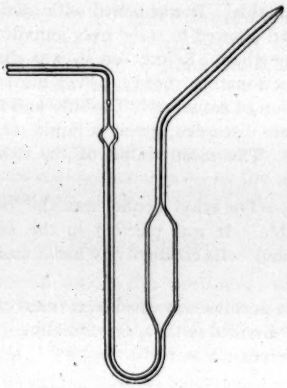


Fig. II.

perature before making up the mixture. On mixing acetone and water, contraction took place and heat was generated, so that the mixture was brought to the temperature before diluting to the mark.

The mother-solution was made by weighing into a measuring-flask the exact amount of salt required and adding the mixed solvent. Since, however, heat was again generated, especially with the calcium nitrate, the solution was again brought to the designated temperature before diluting to the mark.

From the mother-solution the other solutions were made by successive dilution. Where this would necessitate the use of small quantities of solution, a new mother-solution was made, and from this successive dilutions prepared.

Solvents.

Water.—The water was purified by the method of Jones and Mackay[1] and had a conductivity of 1×10^{-6} at 0°.

Methyl Alcohol.—The methyl alcohol was the best commercial article obtainable. It was boiled with calcium oxide for a day, distilled and allowed to stand over anhydrous copper sulphate for a long time. Before use it was distilled, using a Linnemann fractionating head. Precautions were taken against absorption of moisture. The first and last portions of the distillate were discarded, giving a liquid which boiled constantly at 66°. The mean value of the conductivity was 2×10^{-6} at 25°.

Ethyl Alcohol.—The ethyl alcohol was the best commercial alcohol obtainable. It was purified in the same manner as the methyl alcohol. Its conductivity had a mean value of 2×10^{-6} at 25°.

Acetone.—The acetone was dried over fused calcium chloride for weeks and distilled with a fractionating head as above. Its conductivity was 0.6×10^{-6}.

Conductivity Measurements.

In all determinations of conductivity at least three different resistances were used, and the values given are the mean. However, if the readings did not agree to 0.1 of 1 per cent, they were usually repeated. The constants of the cells were checked at frequent intervals. The cells were not allowed to remain in contact with the solution when not in use, nor to remain empty after being dried out with alcohol and ether. In the former case, small quantities of salt were found to be slowly absorbed and in the latter acetic acid was formed by the action of the platinum on the alcohol or ether in the presence of air. When not in use the cells were filled with pure distilled water.

A N/50 and a N/500 solution of potassium chloride were used in determining the cell constants. The conductivity of the former was taken as 129.7, at 25°. The value of the lat-

[1] Z. physik. Chem., 22, 237 (1897). THIS JOURNAL, 19, 91 (1897).

ter was determined several times in different cells. The mean value obtained agrees well with the interpolated values of other observers.

Table V.—Conductivity of N/500 Potassium Chloride at 25°.

Observed value corrected for the conductivity of water	136.5
Corresponding value obtained by Jones and West[1]	135.5
Deduced value, from Kohlrausch[2]	136.94
Interpolated value, from Ostwald[3]	138.7

The temperature coefficients are obtained by dividing the increase in the conductivity per degree, by the conductivity at the lower temperature.

Lithium Nitrate.

The lithium nitrate used in this work was a sample obtained from Kahlbaum. No appreciable impurity could be detected. It was dried in an air-bath at 150° until the weight remained constant. The salt was kept in a desiccator. The operation of drying was repeated whenever the salt was exposed to the air.

Table VI.—Conductivity of Lithium Nitrate in Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	31.17	43.05	0.0154
10	37.62	51.31	0.0145
25	43.40	60.49	0.0158
50	48.31	67.2	0.0157
100	52.0	72.6	0.0155
200	55.1	76.8	0.0147
400	56.8	80.0	0.0172
800	59.6	83.7	0.0162
1200	60.8	85.3	0.0160
1600	61.9	86.7	0.0160

[1] THIS JOURNAL, 34, 357 (1905).
[2] Leitvermögen der Elektrolyten.
[3] Lehrbuch der allgemeinen Chem., 2d Ed., p. 732.

Table VII.—Conductivity of Lithium Nitrate in a Mixture of 25 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°	Temperature coefficients.
5	33.50	44.27	0.0128
10	40.78	53.85	0.0128
25	48.36	64.63	0.0134
50	54.29	72.8	0.0136
100	58.9	79.8	0.0148
200	63.6	85.9	0.0140
400	66.2	90.6	0.0147
800	69.8	95.7	0.0148
1200	71.0	97.7	0.0150
1600	73.1	99.8	0.0146

Table VIII.—Conductivity of Lithium Nitrate in a Mixture of 50 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	32.79	41.26	0.0103
10	41.11	51.68	0.0100
25	51.38	65.39	0.0109
50	58.82	75.42	0.0113
100	65.2	84.8	0.0120
200	69.6	93.2	0.0135
400	75.2	99.2	0.0128
800	80.0	105.3	0.0127
1200	83.3	109.6	0.0126
1600	86.8	112.2	0.0117

Table IX.—Conductivity of Lithium Nitrate in a Mixture of 75 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	25.53	29.98	0.00703
10	34.06	39.45	0.0158
25	45.86	53.69	0.00683
50	55.50	66.30	0.0078
100	65.2	78.4	0.0081
200	74.8	92.2	0.0093
400	82.6	103.0	0.0099
800	90.0	113.3	0.0103
1200	94.4	119.0	0.0104
1600	96.6	123.6	0.0112

Table X.—Conductivity of Lithium Nitrate in Acetone at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	7.78	9.25	0.00755
10	9.67	10.87	0.00493
25	11.35	12.86	0.00532
50	14.07	15.64	0.00447
100	18.1	19.5	0.00310
200	23.8	25.3	0.00252
400	30.6	32.4	0.00232
800	43.4	45.5	0.00193
1200	48.7	52.5	0.00311
1600	55.3	59.8	0.00325

Table XI.—Comparison of the Conductivities of Lithium Nitrate in Mixtures of Acetone and Methyl Alcohol at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	31.17	33.50	32.79	25.53	7.78
10	37.62	40.78	41.11	34.06	9.67
25	43.40	48.36	51.38	45.86	11.35
50	48.31	54.29	58.82	55.50	14.07
100	52.0	58.9	65.2	65.2	18.1
200	55.1	63.6	69.6	74.8	23.8
400	56.8	66.2	75.2	82.6	30.6
800	59.6	69.8	80.0	90.0	43.4
1200	60.8	71.0	83.3	94.4	48.7
1600	61.9	73.1	86.8	96.6	55.3

Table XII.—Comparison of the Conductivities of Lithium Nitrate in Mixtures of Acetone and Methyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	43.05	44.27	41.26	29.98	9.25
10	51.31	53.85	51.68	39.45	10.87
25	60.49	64.63	65.39	53.69	12.86
50	67.2	72.8	75.42	66.30	15.64
100	72.6	79.8	84.8	78.4	19.5
200	76.8	85.9	93.2	92.2	25.3
400	80.0	90.6	99.2	103.0	32.4
800	83.7	95.7	105.3	113.3	45.5
1200	85.3	97.7	109.6	119.0	52.5
1600	86.7	99.8	112.2	123.6	59.8

Table XIII.—Comparison of the Temperature Coefficients of Conductivity of Lithium Nitrate in Mixtures of Acetone and Methyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent
5	0.0152	0.0129	0.0103	0.00703	0.00755
10	0.0145	0.0128	0.0100	0.00158	0.00493
25	0.0158	0.0134	0.0109	0.00683	0.00532
50	0.0157	0.0136	0.0113	0.0078	0.00447
100	0.0155	0.0148	0.0120	0.0081	0.00310
200	0.0147	0.0140	0.0135	0.0093	0.00252
400	0.0172	0.0147	0.0128	0.0099	0.00232
800	0.0162	0.0148	0.0127	0.0103	0.00192
1200	0.0160	0.0150	0.0126	0.0104	0.00311
1600	0.0160	0.0146	0.0117	0.0118	0.00325

Tables VI. to XIII. (Figs. III. and IV.) show that lithium nitrate, in mixtures of methyl alcohol and acetone, gives a pronounced maximum in conductivity. At high concentrations the maximum is rather small. As the dilution is in-

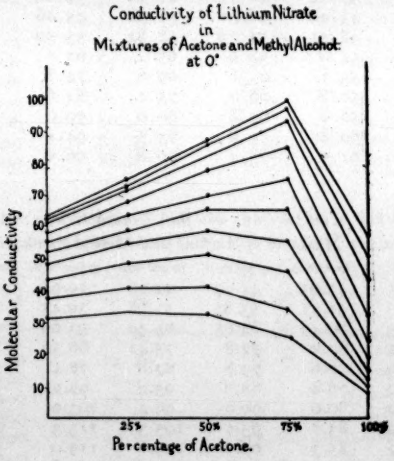


Fig. III.

creased the maximum appears in the 75 per cent mixture and even beyond. It should also be noticed that, in the dilute

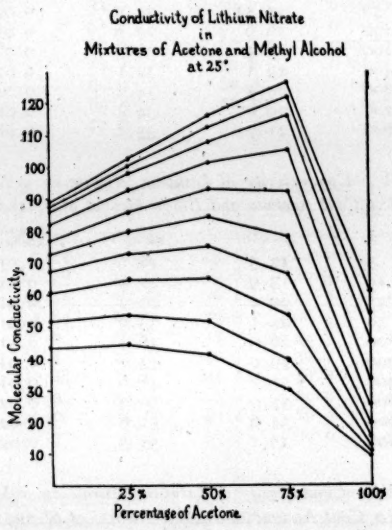


Fig. IV.

solutions, the rise in conductivity is directly proportional to the amount of acetone, up to the 75 per cent mixture. The maximum is increased by rise in temperature.

The points will be made clear by a study of the figures. In all cases the curves represent the molecular conductivities at the successive dilutions.

Table XIV.—Conductivity of Lithium Nitrate in Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	9.14	14.65	0.0241
10	10.75	17.17	0.0238
25	13.55	21.71	0.0240
50	15.54	24.9	0.0241
100	16.9	27.6	0.0251
200	18.4	30.3	0.0260
400	19.1	32.1	0.0271
800	20.3	34.1	0.0251
1200	20.0	34.4	0.0288
1600	21.7	35.4	0.0252

Table XV.—Conductivity of Lithium Nitrate in a Mixture of 25 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	12.5	18.6	0.0195
10	15.9	22.9	0.0176
25	20.2	29.2	0.0178
50	23.1	33.9	0.0187
100	26.0	38.4	0.0191
200	29.0	43.2	0.0196
400	31.2	46.6	0.0198
800	33.0	50.3	0.0210
1200	34.6	51.8	0.0222
1600	35.1	54.5	0.0220

Table XVI.—Conductivity of Lithium Nitrate in a Mixture of 50 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	15.2	19.7	0.0142
10	19.6	25.4	0.0119
25	26.1	33.8	0.0118
50	30.9	40.4	0.0123
100	35.7	47.6	0.0133
200	40.4	54.8	0.0142
400	44.4	61.3	0.0152
800	47.4	67.0	0.0165
1200	49.4	69.6	0.0164
1600	50.7	71.9	0.0167

Table XVII.—Conductivity of Lithium Nitrate in a Mixture of 75 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	14.1	16.9	0.00795
10	19.3	22.5	0.0066
25	27.2	31.3	0.0060
50	34.3	39.7	0.0063
100	41.7	49.6	0.0074
200	50.2	60.1	0.0079
400	54.2	70.8	0.0122
800	64.9	80.9	0.0098
1200	69.5	86.5	0.0098
1600	70.6	91.7	0.0119

Table XVIII.—Comparison of the Conductivities of Lithium Nitrate in Mixtures of Acetone and Ethyl Alcohol at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	9.14	12.5	15.2	14.1	7.78
10	10.75	15.9	19.6	19.3	9.67
25	13.55	20.2	26.1	27.2	11.35
50	15.54	23.1	30.9	34.3	14.07
100	16.9	26.0	35.7	41.7	18.1
200	18.4	29.0	40.4	50.2	23.8
400	19.1	31.2	44.4	54.2	30.6
800	20.3	33.0	47.4	64.9	43.4
1200	20.0	34.6	49.4	69.5	48.7
1600	21.7	35.1	50.7	70.6	55.3

Table XIX.—Comparison of the Conductivities of Lithium Nitrate in Mixtures of Acetone and Ethyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	14.65	18.6	19.7	16.9	9.25
10	17.17	22.9	25.4	22.5	10.87
25	21.71	29.2	33.8	31.3	12.86
50	24.90	33.9	40.4	39.7	15.64
100	27.60	38.4	47.6	49.6	19.5
200	30.3	43.2	54.8	60.1	25.3
400	32.1	46.6	61.3	70.8	32.4
800	34.1	50.3	67.0	80.9	45.5
1200	34.4	51.8	69.6	86.5	52.5
1600	35.4	54.5	71.9	91.7	59.8

Table XX.—Comparison of the Temperature Coefficients of Conductivity of Lithium Nitrate in Mixtures of Acetone and Ethyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	0.0241	0.0195	0.0142	0.00795	0.00755
10	0.0238	0.0176	0.0119	0.0066	0.00493
25	0.0240	0.0178	0.0118	0.0060	0.00532
50	0.0241	0.0187	0.0123	0.0063	0.00447
100	0.0251	0.0191	0.0133	0.0074	0.00310
200	0.0260	0.0196	0.0142	0.0079	0.00252
400	0.0271	0.0198	0.0152	0.0122	0.00232
800	0.0251	0.0210	0.0165	0.00985	0.00192
1200	0.0288	0.0222	0.0164	0.0098	0.00311
1600	0.0252	0.0220	0.0167	0.0119	0.00325

Tables XIV. to XX. (Figs. V. and VI.) show the same characteristics for lithium nitrate, in mixtures of acetone and

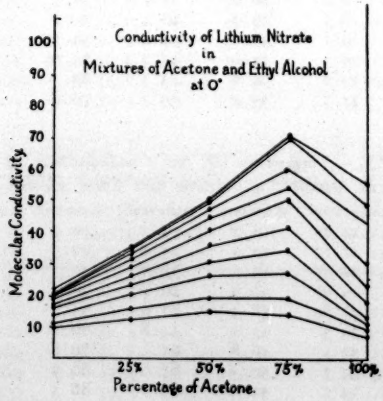


Fig. V.

ethyl alcohol, as those observed for the same salt in mixtures

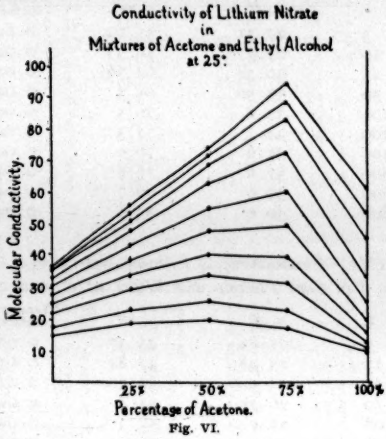


Fig. VI.

of acetone and methyl alcohol, but there is not such a well-defined maximum in these curves.

Table XXI.—Conductivity of Lithium Nitrate in Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	44.45	80.72	0.0323
10	46.39	83.87	0.0323
25	49.57	91.4	0.0334
50	51.4	94.4	0.0334
100	52.5	97.0	0.0340
200	53.1	98.8	0.0342
400	54.3	100.8	0.0341
800	55.0	102.0	0.0340
1200	55.9	102.6	0.0332
1600	56.3	102.8	0.0330
	(58.3)	(107.0)	

Table XXII.—Conductivity of Lithium Nitrate in a Mixture of 25 Per Cent Acetone and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	27.31	55.69	0.0415
10	27.37	56.35	0.0421
25	30.32	62.76	0.0427
50	31.50	65.3	0.0430
100	32.8	70.5	0.0460
200	34.1	72.5	0.0450
400	34.6	76.0	0.048
800	37.6	77.8	0.043
1200	39.0	80.7	0.0425
1600	40.0	83.1	0.0430

Table XXIII.—Conductivity of Lithium Nitrate in a Mixture of 50 Per Cent Acetone and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	21.81	43.37	0.0394
10	23.48	47.84	0.0415
25	24.90	51.33	0.0425
50	26.26	54.4	0.0427
100	27.2	57.3	0.0442
200	29.1	60.0	0.0425
400	28.8	60.0	0.0433
800	29.9	62.7	0.0440
1200	31.6	65.9	0.0425
1600	32.3	67.5	0.0435

Table XXIV.—Conductivity of Lithium Nitrate in a Mixture of 75 Per Cent Acetone and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	21.25	36.78	0.0292
10	24.41	42.65	0.0298
25	27.64	48.92	0.0308
50	30.25	54.14	0.0316
100	31.8	57.4	0.0322
200	33.5	61.4	0.0333
400	35.1	63.6	0.0325
800	36.7	66.3	0.0322
1200	38.1	68.6	0.0320
1600	37.8	69.1	0.0331

Table XXV.—Comparison of the Conductivities of Lithium Nitrate in Mixtures of Acetone and Water at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	44.45	27.31	21.81	21.25	7.78
10	46.39	27.37	23.48	24.41	9.67
25	49.57	30.32	24.90	27.64	11.35
50	51.4	31.50	26.26	30.25	14.07
100	52.5	32.8	27.2	31.8	18.1
200	54.8	34.1	29.1	33.5	23.8
400	54.3	34.6	28.8	35.1	30.6
800	55.0	37.6	29.9	36.7	43.4
1200	55.9	39.0	31.6	38.1	48.7
1600	56.3	40.0	32.3	37.8	55.3

Table XXVI.—Comparison of the Conductivities of Lithium Nitrate in Mixtures of Acetone and Water at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	80.72	55.69	43.37	36.78	9.25
10	83.87	56.35	47.84	42.65	10.87
25	91.4	62.74	51.33	48.92	12.86
50	94.4	65.3	54.4	54.14	15.64
100	97.0	70.5	57.3	57.4	19.5
200	98.8	72.5	60.0	61.4	25.3
400	100.8	76.0	60.0	63.6	32.4
800	102.0	77.8	62.7	66.3	45.5
1200	102.6	80.7	65.9	68.6	52.5
1600	102.8	83.1	67.5	69.1	59.8

Table XXVII.—Comparison of the Temperature Coefficients of Conductivity of Lithium Nitrate in Mixtures of Acetone and Water from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	0.0323	0.0415	0.0394	0.0292	0.00755
10	0.0323	0.0423	0.0415	0.0298	0.00493
25	0.0334	0.0427	0.0425	0.0308	0.00532
50	0.0334	0.0430	0.0427	0.0316	0.00447
100	0.0340	0.0460	0.0442	0.0322	0.00310
200	0.0342	0.0450	0.0425	0.0333	0.00252
400	0.0341	0.048	0.0433	0.0325	0.00232
800	0.0340	0.043	0.0440	0.0322	0.00192
1200	0.0332	0.0425	0.0425	0.0320	0.00311
1600	0.0330	0.0430	0.0435	0.0331	0.00325

Tables XXI. to XXVII. (Figs. VII. and VIII.) for lithium

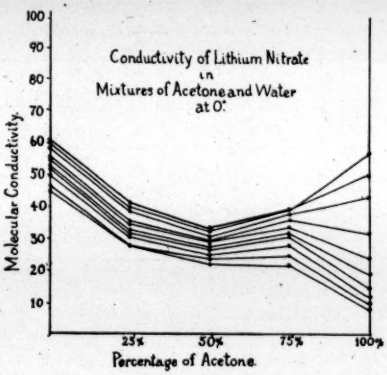


Fig. VII.

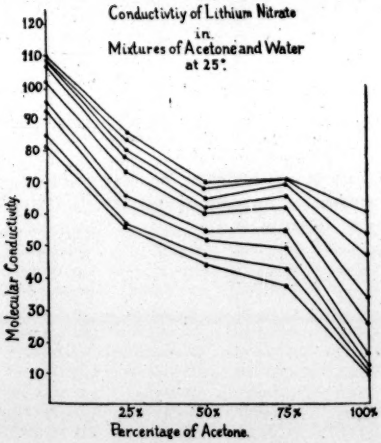


Fig. VIII.

nitrate, in mixtures of acetone and water show, at low temperatures and at high dilution, the minimum which is familiar under similar circumstances in mixtures of the alcohols and water. There is, however, even in this case, a tendency towards a maximum, which results in an inflection-point in most of the curves. It should be especially noticed that the curves diverge from each other rapidly, between the 75 per cent mixture and pure acetone. This seems to indicate that the dissociation is greatly increased by the addition of small amounts of water.

Potassium Iodide.

The salt gave no test for the presence of an iodate and the flame test showed no appreciable impurity. The salt was dried at 100°–110° and kept in a desiccator. The salt dissolved in acetone, giving only a very slight coloration.

Table XXVIII.—Conductivity of Potassium Iodide in Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	65.7	91.4	0.0156
300	68.1	94.6	0.0156
400	68.8	96.3	0.0159
600	70.1	99.0	0.0165
800	70.6	100.5	0.0169
1000	71.1	101.9	0.0174
1200	71.4	102.4	0.0174
1600	71.7	103.3	0.0176

Table XXIX.—Conductivity of Potassium Iodide in a Mixture of 25 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	74.1	101.5	0.0148
300	75.6	103.7	0.0151
400	77.6	106.1	0.0147
600	78.1	108.8	0.0157
800	82.3	113.4	0.0151
1000	80.8	113.8	0.0163
1200	82.8	113.8	0.0149
1600	83.9	116.5	0.0155

Table XXX.—Conductivity of Potassium Iodide in a Mixture of 50 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	82.7	110.3	0.0133
300	85.2	114.7	0.0139
400	87.2	114.8	0.0127
600	89.6	118.6	0.0129
800	91.9	121.8	0.0130
1000	93.6	123.1	0.0126
1200	93.7	126.2	0.0139
1600	94.1	129.2	0.0149

Table XXXI.—Conductivity of Potassium Iodide in a Mixture of 75 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	93.1	117.0	0.0103
300	95.6	123.0	0.0115
400	97.8	124.3	0.0108
600	100.4	129.0	0.0110
800	104.1	131.8	0.0106
1000	103.7	132.7	0.0120
1200	104.3	135.7	0.0118
1600	106.5	137.7	0.0117

Table XXXII.—Conductivity of Potassium Iodide in Acetone at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	100.4	118.0	0.00701
300	105.8	126.2	0.00772
400	108.9	128.7	0.00730
600	112.3	134.1	0.00775
800	116.2	138.6	0.00772
1000	118.4	141.6	0.00785
1200	118.2	140.3	0.00750
1600	120.0	141.1	0.00704

Table XXXIII.—Comparison of the Conductivities of Potassium Iodide in Mixtures of Acetone and Methyl Alcohol at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	65.7	74.1	82.7	93.1	100.4
300	68.1	75.6	85.2	95.6	105.8
400	68.8	77.6	87.2	97.8	108.9
600	70.1	78.1	89.6	100.4	112.3
800	70.6	82.3	91.9	104.1	116.2
1000	71.1	80.8	93.6	103.7	118.4
1200	71.4	82.8	93.7	104.3	118.2
1600	71.7	83.9	94.1	106.5	120.0

Table XXXIV.—Comparison of the Conductivities of Potassium Iodide in Mixtures of Acetone and Methyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	91.4	101.5	110.3	117.0	118.0
300	94.6	103.7	114.7	123.0	126.2
400	96.3	106.1	114.8	124.3	128.7
600	99.0	108.8	118.6	129.0	134.1
800	100.5	113.4	121.8	131.8	138.6
1000	101.9	113.8	123.1	132.7	141.6
1200	102.4	113.8	126.2	135.7	140.3
1600	103.3	116.5	129.2	137.7	141.1

Table XXXV.—Comparison of the Temperature Coefficients of Conductivity of Potassium Iodide in Mixtures of Acetone and Methyl Alcohol from 0° to 25°.

v_{25}	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	0.0156	0.0148	0.0133	0.0103	0.00701
300	0.0156	0.0151	0.0139	0.0115	0.00772
400	0.0159	0.0147	0.0127	0.0108	0.00730
600	0.0165	0.0157	0.0129	0.0110	0.00775
800	0.0169	0.0151	0.0130	0.0106	0.00772
1000	0.0173	0.0163	0.0126	0.0120	0.00785
1200	0.0174	0.0149	0.0159	0.0118	0.00750
1600	0.0176	0.0155	0.0149	0.0117	0.00704

Tables XXVIII. to XXXV. (Figs IX. and X.) for potassium iodide, in mixtures of acetone and methyl alcohol, show that the conductivity is almost exactly what we should expect

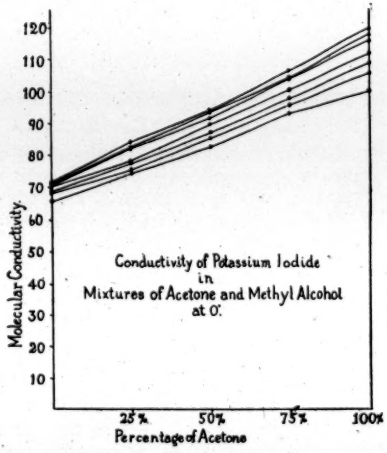


Fig. IX.

from the law of averages. There is, however, a slight tendency toward a maximum as we raise the temperature. In this respect the results are similar to those obtained with lithium nitrate. The values for the conductivity of potassium

iodide in pure water and in ethyl and methyl alcohols were taken from the work of Jones and Lindsay.

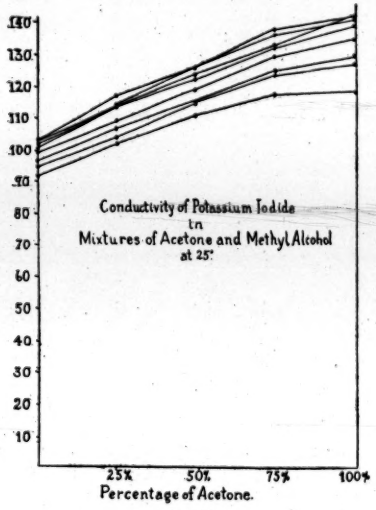


Fig. X.

Table XXXVI.—Conductivity of Potassium Iodide in Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	22.0	34.6	0.0230
300	23.2	36.5	0.0241
400	23.8	37.3	0.0238
600	25.5	39.1	0.0212
800	26.2	39.9	0.0209
1000	27.3	41.2	0.0202
1200	27.9	41.8	0.0200
1600	28.6	42.8	0.0194

Table XXXVII.—Conductivity of Potassium Iodide in a Mixture of 25 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	35.5	52.5	0.0192
300	36.4	54.2	0.0196
400	37.8	56.3	0.0196
600	38.8	58.0	0.0197
800	40.3	60.5	0.0200
1000	39.8	59.7	0.0200
1200	39.7	60.8	0.0212
1600	40.1	63.5	0.0232

Table XXXVIII.—Conductivity of Potassium Iodide in a Mixture of 50 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	52.2	71.4	0.0146
300	53.4	74.0	0.0155
400	56.1	76.8	0.0148
600	57.5	79.1	0.0150
800	59.5	82.6	0.0155
1000	59.7	82.9	0.0155
1200	59.8	82.9	0.0154
1600	61.3	85.4	0.0157

Table XXXIX.—Conductivity of Potassium Iodide in a Mixture of 75 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	72.0	92.7	0.0115
300	75.3	97.5	0.0118
400	78.0	100.1	0.0113
600	79.5	102.4	0.0115
800	82.4	106.0	0.0114
1000	81.8	105.4	0.0115
1200	82.7	107.1	0.0118
1600	84.8	109.0	0.0114

Table XL.—Comparison of the Conductivities of Potsasium Iodide in Mixtures of Acetone and Ethyl Alcohol at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	22.0	35.5	52.2	72.0	100.4
300	23.2	36.4	53.4	75.3	105.8
400	23.8	37.8	56.1	78.0	108.9
600	25.5	38.8	57.5	79.5	112.3
800	26.2	40.3	59.5	82.4	116.2
1000	27.3	39.8	59.7	81.8	118.4
1200	27.9	39.7	59.8	82.7	118.2
1600	28.6	40.1	61.3	84.8	120.0

Table XLI.—Comparison of the Conductivities of Potassium Iodide in Mixtures of Acetone and Ethyl Alcohol at 0° and 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	34.6	52.5	71.4	92.7	118.0
300	36.5	54.2	74.0	97.5	126.2
400	37.3	56.3	76.8	100.1	128.7
600	39.1	58.0	79.1	102.4	134.1
800	39.9	60.5	82.6	106.0	138.6
1000	41.2	59.7	82.9	105.4	141.6
1200	41.8	60.8	82.9	107.1	140.3
1600	42.8	63.5	85.4	109.0	141.1

Table XLII.—Comparison of the Temperature Coefficients of Conductivity of Potassium Iodide in Mixtures of Acetone and Ethyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	0.0230	0.0192	0.0146	0.0115	0.00701
300	0.0241	0.0196	0.0155	0.0118	0.00772
400	0.0238	0.0196	0.0148	0.0113	0.00730
600	0.0212	0.0197	0.0150	0.0115	0.00775
800	0.0209	0.0200	0.0155	0.0114	0.00772
1000	0.0202	0.0200	0.0155	0.0115	0.00785
1200	0.0200	0.0212	0.0154	0.0118	0.00750
1600	0.0194	0.0232	0.0157	0.0114	0.00704

Tables XXXVI. to XLII. (Figs. XI. and XII.) show the same characteristics for potassium iodide, in mixtures of acetone and ethyl alcohol, as those observed for the same salt in

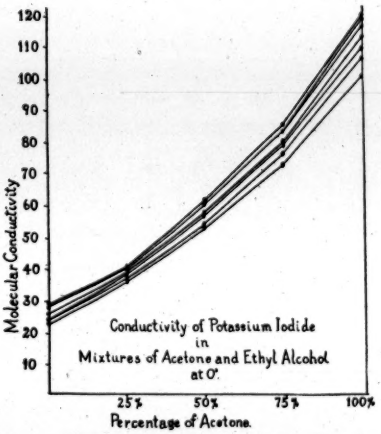


Fig. XI.

mixtures of acetone and methyl alcohol, but there is less of a tendency towards a maximum. In fact, there is a slight sagging in the curves. It is observed that this statement is

almost identical with the one in regard to lithium nitrate in mixtures of acetone and ethyl alcohol (p. 505).

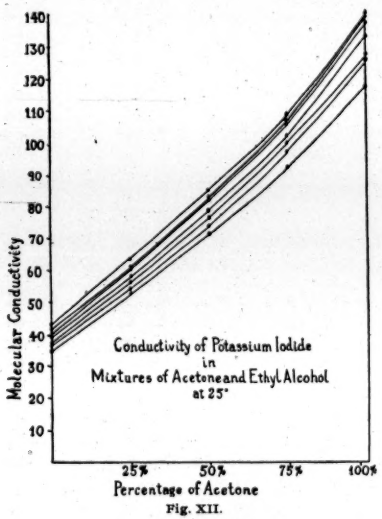


Fig. XII.

Table XLIII.—Conductivity of Potassium Iodide in Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	76.7	136.3	0.0310
300	77.2	138.3	0.0316
400	77.5	138.8	0.0318
600	78.0	139.8	0.0312
800	78.0	140.1	0.0318
1000	78.0	140.6	0.0320
1200	78.0	140.7	0.0322
1600	78.0	140.7	0.0322

Table XLIV.—Conductivity of Potassium Iodide in a Mixture of 25 Per Cent Acetone and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	44.6	91.1	0.0392
300	44.7	92.7	0.0430
400	45.3	92.4	0.0416
600	46.1	95.6	0.0430
800	47.0	96.9	0.0425
1000	46.3	96.2	0.0432
1200	47.5	102.9	0.0485
1600	47.8	100.1	0.0438

Table XLV.—Conductivity of Potassium Iodide in a Mixture of 50 Per Cent Acetone and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	36.3	73.8	0.0413
300	36.8	75.9	0.0425
400	37.2	76.3	0.0420
600	37.6	77.7	0.0427
800	38.6	79.4	0.0423
1000	39.0	80.9	0.0430
1200	38.4	80.6	0.0439
1600	37.5	78.8	0.0440

Table XLVI.—Conductivity of Potassium Iodide in a Mixture of 75 Per Cent Acetone and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	41.6	74.1	0.0311
300	41.9	74.1	0.0308
400	42.2	74.6	0.0304
600	42.8	75.4	0.0302
800	43.7	79.7	0.0330
1000	42.2	76.4	0.0320
1200	42.8	76.1	0.0310
1600	44.1	79.7	0.0321

Table XLVII.—Comparison of the Conductivities of Potassium Iodide in Mixtures of Acetone and Water at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	76.7	44.6	36.3	41.6	100.4
300	77.2	44.7	36.8	41.9	105.8
400	77.5	45.3	37.2	42.2	108.9
600	78.0	46.1	37.6	42.8	112.3
800	78.0	47.0	38.6	43.7	116.2
1000	78.0	46.3	39.0	42.4	118.4
1200	78.0	47.5	38.4	42.8	118.2
1600	78.0	47.8	37.5	44.1	120.0

Table XLVIII.—Comparison of the Conductivities of Potassium Iodide in Mixtures of Acetone and Water at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	136.3	91.1	73.8	74.1	118.0
300	138.3	92.7	75.9	74.1	126.2
400	138.8	92.4	76.3	74.6	128.7
600	139.8	95.6	77.7	75.4	134.1
800	140.1	96.9	79.4	79.7	138.6
1000	140.6	96.2	80.9	76.4	141.6
1200	140.7	102.9	80.6	76.1	140.3
1600	140.7	100.1	78.8	79.7	141.1

Table XLIX.—Comparison of the Temperature Coefficients of Conductivity of Potassium Iodide in Mixtures of Acetone and Water from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	0.0310	0.0392	0.0413	0.0311	0.00701
300	0.0316	0.0430	0.0425	0.0308	0.00772
400	0.0318	0.0416	0.0420	0.0304	0.00730
600	0.0312	0.0430	0.0427	0.0302	0.00775
800	0.0318	0.0425	0.0423	0.0330	0.00772
1000	0.0320	0.0432	0.0430	0.0320	0.00785
1200	0.0322	0.0485	0.0439	0.0310	0.00750
1600	0.0322	0.0438	0.0440	0.0321	0.00704

Tables XLIII. to XLIX. (Figs. XIII. and XIV.) for potassium iodide, in mixtures of acetone and water, display a minimum in molecular conductivity. There is no tendency towards

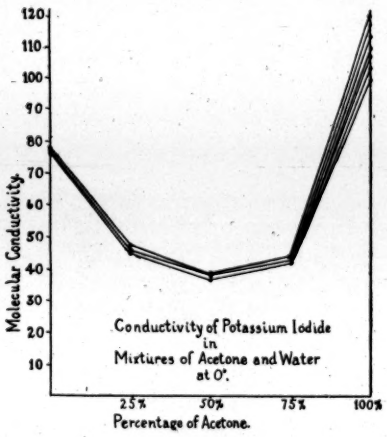


Fig. XIII.

a maximum. It should, however, be noticed that the divergence of the curves between the 75 per cent mixture and pure acetone is small. The salt is, therefore, quite largely dissociated at all dilutions in all of the mixtures.

It was thought advisable, at this stage, to use solutions of sodium iodide in the various mixtures. Solutions of sodium iodide in acetone had been investigated by Carrara,[1] Dutoit and Friderich[2] and by Jones.[3] It was noticed, however, that

[1] Gazz. chim. ital., [1], 27, 207 (1897).
[2] Bull. Soc. Chim., [3], 19, 334 (1898).
[3] This Journal, 27, 16 (1902).

the solution had a high coloration, which deepened on standing. Moreover, there was a slight deposit formed at the same time. On evaporation the residue was still colored. The strongest solutions of the sodium iodide, in acetone, gave a

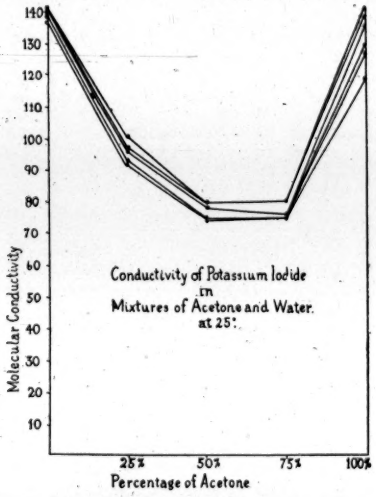


Fig. XIV.

test for iodine with starch paste, while the more dilute solutions, though still somewhat colored, gave none. Free iodine was then added to pure acetone until the same color was reproduced. This solution, tested with starch paste, gave no test for iodine. Time did not permit the further investigation of this interesting point.

Calcium Nitrate.

The calcium nitrate used was an anhydrous preparation obtained from Kahlbaum. It was heated for several days at

140°, until it had a constant weight. Subsequently, it was dried for some time at 140° after each exposure to the air. The salt then contained no calcium oxide, and showed no appreciable impurity by the flame test.

Table L.—Conductivity of Calcium Nitrate in Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 0°. (Carroll.)	μ_v 25°.	μ_v 25°. (Carroll,)	Temperature coefficients.
5	14.33		19.67		0.0149
10	18.98		25.38		0.0135
16				32.79	
25	27.66		36.77		0.0131
32		31.30		41.88	0.0135
50	34.6		45.7		0.0128
64		37.27		50.79	0.0145
100	42.2		55.9		0.0130
128		46.66		60.52	0.0119
200	49.9		65.4		0.0124
256		55.17		73.98	0.0136
400	58.2		75.6		0.0120
800	65.7		86.6		0.0127
1200	74.4		95.0		0.0111
1600	77.2		98.2		0.0109

Table LI.—Conductivity of Calcium Nitrate in a Mixture of 25 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	13.13	17.36	0.0129
10	17.76	23.08	0.0120
25	26.33	33.74	0.0111
50	33.9	43.2	0.0110
100	42.1	53.9	0.0112
200	50.7	66.8	0.0127
400	60.9	76.8	0.0105
800	71.0	89.4	0.0104
1200	79.7	98.0	0.0092
1600	82.6	102.7	0.0098

Table LII.—Conductivity of Calcium Nitrate in a Mixture of 50 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	10.16	12.97	0.0111
10	13.82	17.29	0.0100
25	21.30	26.11	0.00903
50	28.11	34.44	0.00895
100	35.7	42.8	0.00795
200	45.2	54.8	0.0085
400	55.3	68.3	0.0088
800	66.8	83.0	0.0097
1200	73.5	91.3	0.0097
1600	79.2	98.8	0.0099

Table LIII.—Conductivity of Calcium Nitrate in a Mixture of 75 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	6.07	7.65	0.0104
10	8.10	9.78	0.0083
25	12.40	14.56	0.0070
50	16.29	19.47	0.0078
100	21.65	25.1	0.00635
200	28.5	33.0	0.00630
400	38.1	44.3	0.0065
800	49.2	57.8	0.00698
1200	57.3	66.9	0.0067
1600	64.2	75.1	0.0068

Table LIV.—Conductivity of Calcium Nitrate in Acetone at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	3.93	4.96	0.0105
10	4.44	5.67	0.0111
25	5.06	6.55	0.0118
50	5.34	6.90	0.0117
100	5.48	7.06	0.0115
200	5.93	7.54	0.0109
400	6.69	8.22	0.00916
800	7.93	9.69	0.00884
1200	9.26	11.22	0.00847
1600	10.36	12.62	0.00873

Table LV.—Comparison of the Conductivities of Calcium Nitrate in Mixtures of Acetone and Methyl Alcohol at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	14.33	13.13	10.16	6.07	3.93
10	18.98	17.76	13.82	8.10	4.44
25	27.66	26.33	21.30	12.40	5.06
50	34.6	33.9	28.11	16.29	5.34
100	42.2	42.1	35.7	21.65	5.48
200	49.9	50.7	45.2	28.5	5.93
400	58.2	60.9	55.3	38.1	6.69
800	65.7	71.0	66.8	49.2	7.93
1200	74.4	79.7	73.5	57.3	9.26
1600	77.2	82.6	79.2	64.2	10.36

Table LVI.—Comparison of the Conductivities of Calcium Nitrate in Mixtures of Acetone and Methyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	19.67	17.36	12.97	7.65	4.96
10	25.38	23.08	17.29	9.78	5.67
25	36.77	33.74	26.11	14.56	6.55
50	45.7	43.2	34.44	19.47	6.90
100	55.9	53.9	42.8	25.1	7.06
200	65.4	66.8	54.8	33.0	7.54
400	75.6	76.8	68.3	44.3	8.22
800	86.6	89.4	83.0	57.8	9.69
1200	95.0	98.0	91.3	66.9	11.22
1600	98.2	102.7	98.8	75.1	12.62

Table LVII.—Comparison of the Temperature Coefficients of Conductivity of Calcium Nitrate in Mixtures of Acetone and Methyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	0.0149	0.0129	0.0111	0.0104	0.0105
10	0.0135	0.0120	0.0100	0.0083	0.0111
25	0.0131	0.0111	0.00903	0.0070	0.0118
50	0.0128	0.0110	0.00895	0.0078	0.0117
100	0.0130	0.0112	0.00795	0.0063	0.0115
200	0.0124	0.0127	0.0085	0.0065	0.0109
400	0.0120	0.0105	0.0088	0.0065	0.00916
800	0.0127	0.0104	0.0097	0.00698	0.00884
1200	0.0111	0.0092	0.0097	0.0067	0.00847
1600	0.0109	0.0098	0.0099	0.0068	0.00873

Tables L. to LVII. (Figs. XV. and XVI.) for calcium nitrate, in mixtures of acetone and methyl alcohol, give a pronounced maximum in conductivity at high dilutions. It will

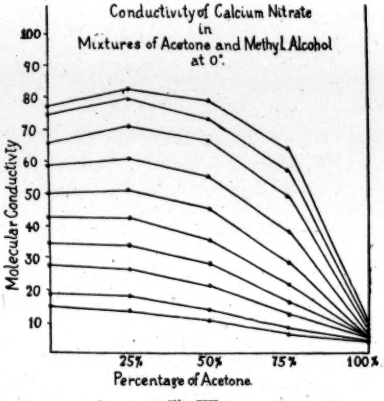


Fig. XV.

be recalled that Jones and Carroll obtained a minimum conductivity with this salt, in mixtures of ethyl alcohol and water, only at low temperatures and at high dilution. It should be noted that calcium nitrate is very slightly dissociated in acetone and that the maximum occurs in the 25 per cent mixture.

The temperature coefficients of conductivity decrease with the dilution, and they are also less in the mixtures than in the

pure solvents, the minimum appearing in the 75 per cent mixture.

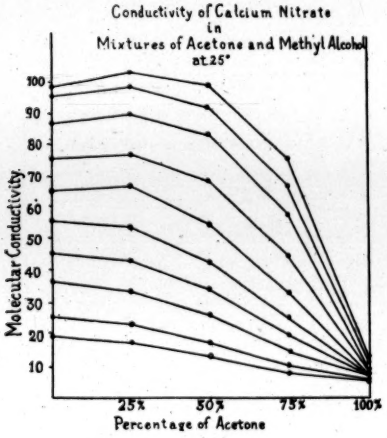


Fig. XVI.

Table LVIII.—Conductivity of Calcium Nitrate in Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	3.80	5.94	0.022
10	5.13	7.86	0.021
25	7.69	11.67	0.020
50	9.80	14.9	0.024
100	11.9	18.4	0.024
200	14.3	22.4	0.024
400	15.2	23.7	0.022
800	17.2	27.5	0.024
1200	18.1	29.5	0.024
1600	18.8	33.3	0.031

Table LIX.—Conductivity of Calcium Nitrate in a Mixture of 25 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	4.45	6.18	0.0156
10	6.01	8.29	0.0151
25	9.29	12.52	0.0140
50	12.20	16.59	0.0144
100	15.4	21.1	0.0148
400	22.3	32.2	0.0177
800	27.2	40.1	0.0190
1200	28.9	42.7	0.0191
1600	31.6	46.3	0.0186

Table LX.—Conductivity of Calcium Nitrate in a Mixture of 50 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	4.42	5.86	0.0130
10	6.00	7.64	0.0109
25	9.25	11.48	0.00963
50	12.33	15.24	0.00945
100	16.1	19.9	0.00942
200	20.7	26.0	0.0102
400	26.1	32.8	0.0102
800	31.8	41.4	0.0121
1200	35.8	46.8	0.0123
1600	38.0	50.7	0.0134

Table LXI.—Conductivity of Calcium Nitrate in a Mixture of 75 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	3.89	5.08	0.0123
10	4.80	5.99	0.00992
25	6.92	8.22	0.00753
50	9.20	11.34	0.00930
100	12.1	13.8	0.0056
200	16.2	18.3	0.0052
400	21.3	24.3	0.00562
800	28.1	32.7	0.0065
1200	33.2	39.1	0.0073
1600	36.2	42.4	0.0068

Table LXII.—Comparison of the Conductivities of Calcium Nitrate in Mixtures of Acetone and Ethyl Alcohol at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	3.80	4.45	4.42	3.89	3.93
10	5.13	6.01	6.00	4.80	4.44
25	7.69	9.29	9.25	6.92	5.06
50	9.80	12.20	12.33	9.20	5.34
100	11.9	15.4	16.1	12.1	5.48
200	14.3	19.1	20.7	16.2	5.93
400	15.2	22.3	26.1	21.3	6.69
800	17.2	27.2	31.8	28.1	7.93
1200	18.1	28.9	35.8	33.2	9.26
1600	18.81	31.6	38.0	36.2	10.36

Table LXIII.—Comparison of the Conductivities of Calcium Nitrate in Mixtures of Acetone and Ethyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	5.94	6.18	5.86	5.08	4.96
10	7.86	8.29	7.64	5.99	5.67
25	11.67	12.52	11.48	8.22	6.55
50	14.91	16.59	15.24	11.34	6.90
100	18.4	21.1	19.9	13.8	7.06
200	22.4	26.5	26.0	18.3	7.54
400	23.7	32.2	32.8	24.3	8.22
800	27.5	40.1	41.4	32.7	9.69
1200	29.5	42.7	46.8	39.1	11.22
1600	33.3	46.3	50.7	42.4	12.62

Table LXIV.—Comparison of the Temperature Coefficients of Conductivity of Calcium Nitrate in Mixtures of Acetone and Ethyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	0.022	0.0156	0.0130	0.0123	0.0105
10	0.021	0.0151	0.0109	0.00992	0.0111
25	0.020	0.0140	0.00963	0.00753	0.0118
50	0.024	0.0144	0.00945	0.00930	0.0117
100	0.024	0.0148	0.00942	0.0056	0.0115
200	0.024	0.0155	0.0102	0.0052	0.0109
400	0.022	0.0177	0.0102	0.00562	0.00916
800	0.024	0.0190	0.0121	0.0065	0.00884
1200	0.024	0.0191	0.0123	0.0073	0.00847
1600	0.031	0.0186	0.0134	0.0068	0.00873

Tables LVIII. to LXIV. (Figs XVII. and XVIII.) for calcium nitrate, in mixtures of acetone and ethyl alcohol, show the same characteristics as were observed in the tables for this

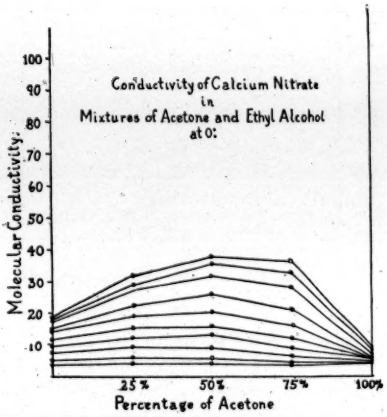


Fig. XVII.

salt in mixtures of acetone and methyl alcohol, but here the maximum is more prominent, being present at all dilutions and at both temperatures. The dissociation of calcium nitrate in ethyl alcohol, however, is small. With increasing dilution the maximum shifts from the 25 per cent mixture to the 75 per cent mixture.

The temperature coefficients in ethyl alcohol are almost constant, perhaps increasing slightly. The temperature coeffi-

cients of the mixtures show a minimum in the 75 per cent mixture. A similar phenomenon was noticed in the mixtures of acetone and methyl alcohol.

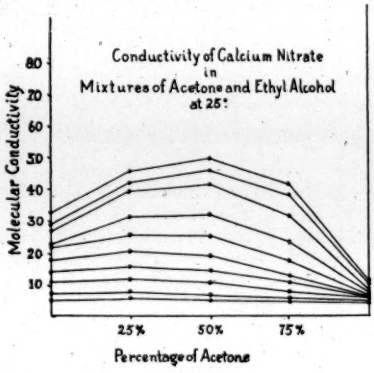


Fig. XVIII.

Table LXV.—Conductivity of Calcium Nitrate in Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	80.3	146.8	0.0331
10	89.8	165.5	0.0333
25	98.2	184.2	0.0350
50	107.0	192.2	0.0313
100	110.4	204.7	0.0341
200	114.9	214.2	0.0343
400	119.9	222.2	0.0341
800	123.4	232.2	0.0351
1200	...	238.5	...
1600	128.3	249.8	0.0378

Table LXVI.—Conductivity of Calcium Nitrate in a Mixture of 25 Per Cent Acetone and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	49.9	101.0	0.0410
10	55.0	112.3	0.0417
25	60.2	123.9	0.0423
50	64.8	134.0	0.0427
100	70.3	144.7	0.0423
200	72.3	154.1	0.0452
400	74.1	154.9	0.0441
800	76.8	161.0	0.0438
1200	79.1	165.4	0.0436
1600	80.0	167.7	0.0439

Table LXVII.—Conductivity of Calcium Nitrate in a Mixture of 50 Per Cent. Acetone and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	36.9	73.4	0.0392
10	42.2	84.6	0.0402
25	46.7	94.8	0.0413
50	50.9	104.7	0.0423
100	54.8	115.4	0.0449
200	59.6	120.3	0.0458
400	61.4	128.0	0.0435
800	64.0	133.1	0.0433
1200	66.1	137.9	0.0434
1600	66.2	139.8	0.0444

Table LXVIII.—Conductivity of Calcium Nitrate in a Mixture of 75 Per Cent Acetone and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	25.0	43.1	0.0290
10	31.3	52.8	0.0272
25	40.1	68.3	0.0281
50	45.8	79.2	0.0291
100	52.6	92.3	0.0300
200	58.4	102.5	0.0301
400	62.6	114.9	0.0331
800	71.6	126.9	0.031
1200	75.1	133.5	0.031
1600	76.7	137.7	0.032

Table LXIX.—Comparison of the Conductivities of Calcium Nitrate in Mixtures of Acetone and Water at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	80.3	49.9	36.9	25.0	3.93
10	89.8	55.0	42.2	31.3	4.44
25	98.2	60.2	46.7	40.1	5.06
50	107.0	64.8	50.9	45.8	5.34
100	110.4	70.3	54.8	52.6	5.48
200	114.9	72.3	59.6	58.4	5.93
400	119.9	74.1	61.4	62.6	6.69
800	123.4	76.8	64.0	71.6	7.93
1200	...	79.1	66.1	75.1	9.26
1600	128.3	80.0	66.2	76.7	10.4

Table LXX.—Comparison of the Conductivities of Calcium Nitrate in Mixtures of Acetone and Water at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	148.6	101.0	73.4	43.1	4.96
10	165.5	112.3	84.6	52.8	5.67
25	184.2	123.9	94.8	68.3	6.55
50	192.2	134.0	104.7	79.2	6.90
100	204.7	144.7	115.4	92.3	7.06
200	214.2	154.1	120.3	102.5	7.54
400	222.2	154.9	128.0	114.9	8.22
800	232.2	161.0	133.1	126.9	9.69
1200	238.5	165.4	137.9	133.5	11.2
1600	249.8	167.7	139.8	137.7	12.6

Table LXXI.—Comparison of the Temperature Coefficients of Conductivity of Calcium Nitrate in Mixtures of Acetone and Water from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent	100 per cent.
5	0.0331	0.0410	0.0392	0.0290	0.0105
10	0.0333	0.0417	0.0402	0.0272	0.0111
25	0.0350	0.0423	0.0413	0.0281	0.0118
50	0.0313	0.0427	0.0423	0.0291	0.0117
100	0.0341	0.0423	0.0449	0.0300	0.0115
200	0.0343	0.0452	0.0458	0.0301	0.0109
400	0.0341	0.0441	0.0435	0.0331	0.00916
800	0.0351	0.0438	0.0433	0.031	0.00884
1200	..	0.0436	0.0434	0.031	0.00847
1600	0.0378	0.0439	0.0444	0.032	0.00873

Tables LXV. to LXXI. (Figs. XIX. and XX.) for calcium nitrate, in mixtures of acetone and water, show a point of inflection at low temperatures and high dilution. In con-

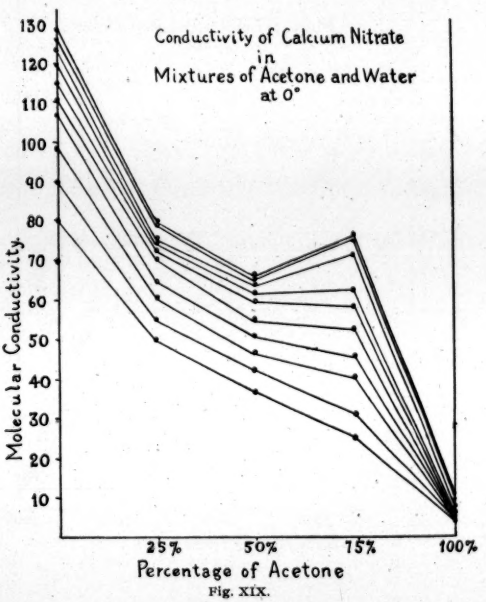


Fig. XIX.

centrated solutions, at high temperatures, the conductivity is what we should expect from the law of averages. These results are similar to those obtained with lithium nitrate in mixtures of acetone and water.

The temperature coefficients of conductivity of water increase with the dilution, while the temperature coefficients of acetone decrease with the dilution. In the 75 per cent mix-

ture the temperature coefficients are nearly independent of the dilution.

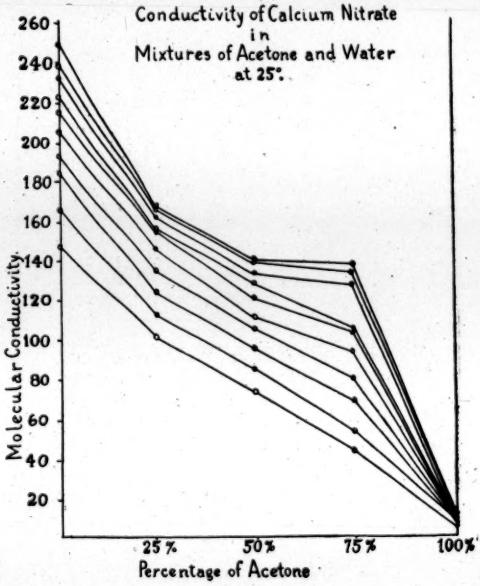


Fig. XX.

Viscosity Measurements.

In the following tables of viscosity data, the values of Thorpe and Rodger[1] for pure water, at 0° and 25°, are taken as the standard and the other values are referred to them ; η represents viscosity, ϕ fluidity and D the density of the liquid in question, at 0° and 25°, compared with the density of water at 0° and 25°, respectively :

[1] Phil. Trans., 185A, 307 (1894.)

Table LXXII.—Fluidity of Water at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
Pure solvent	0.01778	56.24	1.000	0.00891	112.3	1.000	0.0426

Table LXXIII.—Fluidity of a Mixture of 25 Per Cent Acetone and Water at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
Pure solvent	0.0293	34.12	0.9802	0.001276	78.37	0.9710	0.0518

Table LXXIV.—Fluidity of Calcium Nitrate in a Mixture of 50 Per Cent Acetone and Water at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
10				0.01397	71.59	0.948	
1600				0.0133	75.13	0.936	
Pure solvent	0.03027	33.03	0.9522	0.0133	74.96	0.937	0.0508

Table LXXV.—Fluidity of Calcium Nitrate in a Mixture of 75 Per Cent Acetone and Water at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
10				0.009617	104.0	0.892	
1600				0.009019	110.9	0.880	
Pure solvent	0.0170	58.80	0.9023	0.008904	112.3	0.879	0.0364

Table LXXVI.—Fluidity of Calcium Nitrate in Acetone at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
10				0.003544	282.1	0.803	
1600				0.003255	307.3	0.790	
Pure solvent	0.004097	244.1	0.8132	0.003237	308.9	0.788	0.0106

Table LXXVII.—Comparison of the Fluidities of Mixtures of Acetone and Water at 0°.

	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
Pure solvent	56.2	34.12	33.03	58.80	244.1

Table LXXVIII.—Comparison of the Fluidities of Calcium Nitrate in Mixtures of Acetone and Water at 25°

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10			71.59	104.0	282.1
1600			75.13	110.9	307.3
Pure solvent	112.3	78.37	74.96	112.3	308.9

Table LXXIX.—Fluidity of Calcium Nitrate in Methyl Alcohol at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
10				0.006179	161.8	0.804	
1600				0.005543	180.4	0.790	
Pure solvent	0.008185	122.2	0.811	0.005659	176.7	0.790	0.0178

Table LXXX.—Fluidity of Calcium Nitrate in a Mixture of 25 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
10				0.005319	188.0	0.811	
1600				0.004604	217.2	0.790	
Pure solvent	0.006498	153.9	0.816	0.004615	216.7	0.792	0.0163

Table LXXXI.—Fluidity of Calcium Nitrate in a Mixture of 50 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
10				0.004532	220.6	0.816	
1600				0.003926	254.7	0.794	
Pure solvent	0.005336	187.4	0.818	0.003891	257.0	0.794	0.0148

Table LXXXII.—Fluidity of Calcium Nitrate in a Mixture of 75 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
10				0.003909	255.8	0.812	
1600				0.003480	287.3	0.793	
Pure solvent	0.004501	222.2	0.817	0.003446	290.1	0.792	0.0122

Table LXXXIII.—Comparison of the Fluidities of Mixtures of Acetone and Methyl Alcohol at 0°.

0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
122.2	153.9	187.4	222.2	244.1

Table LXXXIV.—Comparison of the Fluidities of Calcium Nitrate in Mixtures of Acetone and Methyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	161.8	188.0	220.6	255.8	282.1
1600	180.4	217.2	254.7	287.3	307.3
Pure solvent	176.7	216.7	257.0	290.1	308.9

Table LXXXV.—Fluidity of Calcium Nitrate in Ethyl Alcohol at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficients.
5				0.01373	72.84	0.81612	
Pure solvent	0.01856	53.88	0.80820	0.01106	90.35	0.7895	0.0271

Table LXXXVI.—Fluidity of Calcium Nitrate in a Mixture of 25 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
5				0.008444	118.4	0.81822	
Pure solvent	0.01041	96.08	0.81244	0.006714	148.9	0.791	0.0220

Table LXXXVII.—Fluidity of Calcium Nitrate in a Mixture of 50 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
5				0.005861	170.6	0.81818	
Pure solvent	0.006801	147.0	0.81394	0.004874	205.2	0.7904	0.0148

Table LXXXVIII.—Fluidity of Calcium Nitrate in a Mixture of 75 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
5				0.004484	223.0	0.81709	
Pure solvent	0.004990	200.4	0.81380	0.003776	264.8	0.7896	0.01296

Table LXXXIX.—Comparison of the Fluidities of Mixtures of Acetone and Ethyl Alcohol at 0°.

0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
53.88	96.08	147.0	200.4	244.1

Table XC.—Comparison of the Fluidities of Calcium Nitrate in Mixtures of Acetone and Ethyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	72.84	118.4	170.6	223.0	263.5
Pure solvent	90.35	148.9	205.2	264.8	308.9

Table XCI.—Comparison of the Temperature Coefficients of Fluidity of Mixtures of Acetone and Water from 0° to 25°.

0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0.0426	0.0518	0.0508	0.0364	0.0106

Table XCII.—Comparison of the Temperature Coefficients of Fluidity of Mixtures of Acetone and Methyl Alcohol from 0° to 25°.

0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0.0178	0.0163	0.0148	0.0122	0.0106

Table XCIII.—Comparison of the Temperature Coefficients of Fluidity of Mixtures of Acetone and Ethyl Alcohol from 0° to 25°.

0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0.0271	0.0220	0.0148	0.01296	0.0106

Tables LXXII. to XCIII. (Figs. XXI. and XXII.) show that

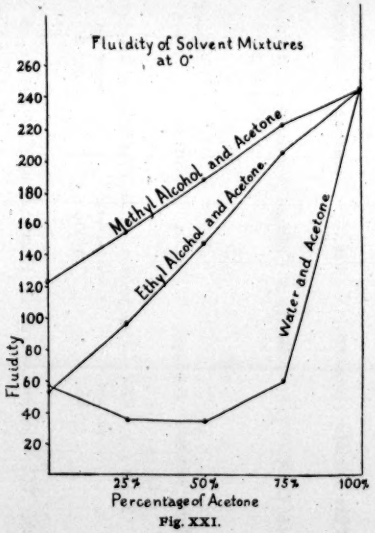


Fig. XXI.

there is a minimum of fluidity only in the case of acetone and water. In the mixtures of acetone with methyl alcohol we get somewhat larger values than would be expected from the

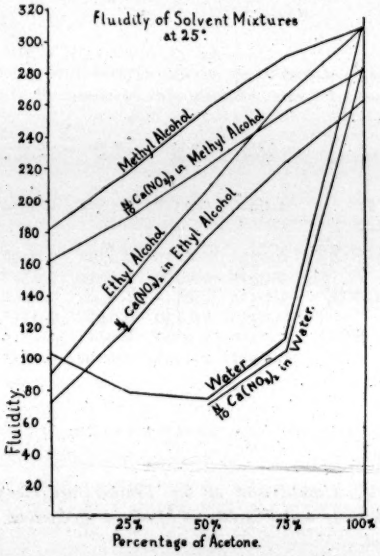


Fig. XXII.

fluidities of the pure solvents. This effect is not so apparent, however, in the case of acetone and ethyl alcohol. These last values were compared with those derived from Dunstan's results[1] and were found to be almost identical with them.

If we compare the viscosity curves of acetone and water with the fluidity curves, we find that the maximum is more pro-

[1] J. Chem. Soc., 85, 821 (1904).

nounced than the fluidity minimum. The viscosity curves for mixtures of acetone and the alcohols show a marked sagging, as Dunstan has pointed out.

Table XCIV.—Comparison of the Temperature Coefficients of Conductivity and Fluidity in Mixtures of Acetone and Water.

v.	Solute.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
Fluidity:						
Pure solv't . . .		0.0426	0.0518	0.0508	0.0364	0.0106
Conductivity:						
5	$Ca(NO_3)_2$	0.0331	0.0410	0.0392	0.0290	0.01050
1600	"	0.0378	0.0439	0.0444	0.0320	0.00873
5	$LiNO_3$	0.0323	0.0415	0.0394	0.0292	0.00755
1600	"	0.0330	0.0430	0.0435	0.0331	0.00325
200	KI	0.0310	0.0392	0.0413	0.0311	0.00701
1600	"	0.0322	0.0438	0.0440	0.0321	0.00704

Table XCV.—Comparison of the Temperature Coefficients of Conductivity and Fluidity in Mixtures of Acetone and Ethyl Alcohol.

v.	Solute.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
Fluidity:						
Pure solv't . . .		0.0271	0.0220	0.0148	0.01296	0.0106
Conductivity:						
5	$Ca(NO_3)_2$	0.022	0.0156	0.0130	0.0123	0.0105
1600	"	0.031(?)	0.0186	0.0134	0.0068	0.00873
5	$LiNO_3$	0.0241	0.0195	0.0142	0.00795	0.00755
1600	"	0.0252	0.0220	0.0167	0.0119	0.00325
200	KI	0.0230	0.0192	0.0146	0.0115	0.00701
1600	"	0.0194	0.0232	0.0157	0.0114	0.00704

Table XCVI.—Comparison of the Temperature Coefficients of Conductivity and Fluidity in Mixtures of Acetone and Methyl Alcohol.

v.	Solute.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
Fluidity:						
Pure solv't	. . .	0.0178	0.0163	0.0148	0.0122	0.0106
Conductivity:						
5	$Ca(NO_3)_2$	0.0149	0.0129	0.0111	0.104	0.0105
1600	"	0.0109	0.0098	0.0099	0.0068	0.00873
5	$LiNO_3$	0.0152	0.0129	0.0103	0.0104	0.00755
1600	"	0.0160	0.0146	0.0117	0.0112	0.00325
200	KI	0.0156	0.0148	0.0133	0.0103	0.00701
1600	"	0.0176	0.0155	0.0149	0.0117	0.00704

Tables XCIV. to XCVI. show that although the temperature coefficients of conductivity and fluidity vary in the same manner, yet the former are uniformly smaller than the latter.

Discussion of Experimental Results.

The curves for the conductivity of potassium iodide in all of the different mixtures, are very similar to the curves of fluidity in the corresponding mixtures. Lithium nitrate and calcium nitrate in all mixtures, at low temperatures, show a deviation from the fluidity curves, particularly in the 75 per cent mixtures, tending to produce a maximum in conductivity.

The work of Jones and Lindsay[1] and of Jones and Carroll[1] showed that solutions of lithium nitrate, in mixtures of methyl alcohol and water, gave curves with a simple minimum, like the fluidity curves for the corresponding mixtures. Calcium nitrate, dissolved in the same mixtures and also in mixtures of ethyl alcohol and water, in no case gave a minimum according to Jones and Carroll,[1] consequently, their curves are not similar to the corresponding fluidity curves.

Our results differ fundamentally from those heretofore observed, in that the mixtures of acetone with the alcohols and water show a tendency towards a maximum in the conductivity of solutions of certain salts, such as lithium nitrate and calcium nitrate.

[1] *Loc. cit.*

PART III.

Discussion of Results.

Since conductivity is dependent upon fluidity, and not *vice versa*, we will first discuss the fluidity curves and then the conductivity curves in connection with them.

When methyl alcohol or ethyl alcohol is mixed with acetone the fluidity curve of the mixtures is a straight line. This is what we should expect, if the fluidity of each of the components has its proportionate effect. Hence, we may conclude that the molecular aggregations of these pure solvents are not essentially changed in regard to size (or symmetry) by mixing the two solvents. We have already shown that the work of Thorpe and Rodger,[1] Traube,[1] Varenne and Godefroy[1] and others has made it evident that viscosity is dependent upon the character of the molecular aggregations present.

It may be objected that a straight line is not the "normal" fluidity curve, since, heretofore, a straight line has been considered to be the normal viscosity curve and the two conceptions are, in general, incompatible. To make this clear, let us suppose that we mix two liquids which are made up of particles which have no unusual action on each other, *i. e.*, do not form new aggregations of any kind. Two monomolecular liquids which do not form complexes on mixing would fulfil this condition. Further, let us suppose that the liquid is allowed to flow through a tube. The resulting fluidity would be the sum of the partial fluidities of the components. That is, the more rapidly moving particles would be held back by the slower ones, and the motion would be a mean value, proportional to the relative amounts of the components. Formulated this would be

$$(m_1 + m_2)\phi = m_1\phi_1 + m_2\phi_2 \ldots\ldots (1),$$

where m_1 and m_2 are the amounts of the components, and ϕ_1 and ϕ_2 are their respective fluidities.

This is similar to the conception which we have in electricity, where the conductance of two or more conductors is

[1] *Loc. cit.*

represented by the sum of their separate conductances. The conductance of a single conductor is expressed by the value

$$\frac{c\ \sigma}{l},$$

where c is the specific conductivity, σ the cross-section of the conductor and l the length. The conductance of a pair of conductors of different material, in parallel, is, per unit length,

$$(\sigma_1 + \sigma_2)c = c_1\sigma_1 + c_2\sigma_2.$$

Admitting this reasoning, it becomes evident that conductivity and fluidity are strictly comparable.

It will be noticed, moreover, that the *viscosities are not additive.*

If η_1 and η_2 represent the viscosities of the two components, then, since viscosity is the reciprocal of fluidity, we have from (1):

$$(m_1 + m_2)\frac{1}{H} = \frac{m_1}{\eta_1} + \frac{m_2}{\eta_2}.$$

By making m_1 and m_2 the percentages of the respective components:

$$\frac{1}{H} = \frac{m_1}{\eta_1} + \frac{1 - m_1}{\eta_2}$$

$$\eta_1\eta_2 = [m_1\eta_2 + (1 - m_1)\eta_1]H$$

$$= [m_1(\eta_2 - \eta_1) + \eta_1]H \quad \ldots\ldots\ldots (2).$$

Now let

$$m_1(\eta_2 - \eta_1) + \eta_1 = m'_1(\eta_2 - \eta_1)$$

then

$$m'_1 = m_1 + \frac{\eta_1}{\eta_2 - \eta_1}.$$

Substituting this value in (2),

$$m'_1 H = \frac{\eta_1\eta_2}{\eta_2 - \eta_1} = \text{constant},$$

which is the equation of the equilateral hyperbola, the Y-axis of which is a distance $\frac{\eta_1}{\eta_2 - \eta_1}$ to the left of the origin, to which equation (1) is referred.

Thus, we seem justified in concluding that *the hyperbola is the normal curve for viscosities.*

From the above considerations we are led to the belief that inferences made from viscosity curves alone may lead to erroneous conclusions. For example, Wijkander[1] reached the conclusion that in no case is the viscosity identical with that calculated by the admixture rule. In the case of mixtures of ether with chloroform and of ether with carbon disulphide, there were inflection-points in the curves, but no simple relation between the viscosity coefficients of a mixture and those of its constituents could be deduced.

Linebarger[2] found that the observed viscosities, in general, were less than those calculated by the mixture rule, except, perhaps, in the case of mixtures of benzene and chloroform and mixtures of carbon disulphide and benzene, toluene, ether and acetic ether, where, according to Dunstan, the temperature of observation, 25°, was possibly too near the boiling-point of the carbon disulphide to make any specific influence which that liquid might exert at lower temperatures perceptible.

Dunstan[3] makes the significant statement that "the law of mixtures is never accurately obeyed, and divergences seem to be more clearly marked in the case of viscosity than with other properties, such as refractive index."

These discrepancies are explained if our view be accepted, since the divergence in every abnormal case thus far investigated is smaller for the fluidity curves than for the corresponding viscosity curves, and the mixtures with carbon disulphide, which give "normal" viscosity curves, also give *fluidity* curves that are equally satisfactory. In the particular case of acetone and methyl alcohol or ethyl alcohol, the fluidity is a straight line, nearly to within the limits of experimental error,

[1] Wied. Beibl., 8, 3 (1879).
[2] Am. J. Sci., [4], 2, 331 (1896).
[3] J. Chem. Soc., 85, 817 (1904). Z. physik. Chem., 49, 590 (1904).

so these two pairs of liquids may be considered as perfectly normal.

It must be stated explicitly that many of the conclusions of the above-mentioned workers are not changed by this new method of comparison of results, especially since, in many cases, they obtained curves with actual maxima and minima. These effects are reproduced in the fluidities as minima and maxima, respectively, which are generally less prominent than before.

A separate paper will be published in the near future, dealing with some of the recorded viscosity data from this new point of view.

When most of the organic solvents worked with up to this time are mixed with water, there is a very large increase in viscosity. In general, there is also a contraction on mixing these solvents and water. Some of those that give a pronounced maximum of viscosity are methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, acetic acid, propionic acid, butyric acid, isobutyric acid and acetone. The workers in this field have attributed the increase in viscosity to increase in the size of the molecular aggregations.

This decrease in fluidity retards the movement of the ions, hence there is a fall in molecular conductivity, which explains the minimum in conductivity heretofore observed by Zelinsky and Krapiwin,[1] Cohen,[1] Jones and Lindsay,[1] Jones and Carroll[1] and ourselves. This relation between viscosity and conductivity, as has been shown, has long been recognized. Wiedemann,[1] Stephan, Dutoit and Friderich and Jones and Carroll have been connected with the development of the exact relation between them.

If the salt happens to be highly dissociated in water and very little dissociated in the other solvent, the curves may be at such an angle with the axis of X that there will be only a sagging of the curve and not an actual minimum. Therefore, the *amount of deviation from the normal curve* appears to us to

[1] *Loc. cit.*

be a matter of prime importance, while the finding of a *minimum* is not.

If we could make a correction at the different parts of the curve for the different degrees of dissociation in the pure solvents and in the mixtures, we should then have a curve exactly parallel to the fluidity curve, if it is true that fluidity and dissociation are the only factors concerned, as Dutoit and Friderich and Jones and Carroll supposed. In our case it is almost impossible to make the correction with the data at hand, except, possibly, in the case of potassium iodide. The conductivity values for potassium iodide show that it is nearly dissociated in all mixtures, but with the other salts complete dissociation is not even approximately reached. Thinking that it might be possible to calculate $\mu\infty$, we have tested Kohlrausch's formula,

$$\frac{\mu\infty - \mu_v}{C^{1/3}} = K,$$

where C is the concentration and K is a constant. We found that it did not apply except in aqueous solutions. Völlmer[1] has already shown that the Ostwald dilution law does not apply to solutions in ethyl alcohol and methyl alcohol. Solutions of potassium iodide, in mixtures of methyl alcohol and water, were investigated by Zelinsky and Krapiwin and Jones and Lindsay. The conductivity curves resemble the fluidity curves for methyl alcohol and water, as shown by Jones and Carroll. We have found the same similarity in the case of potassium iodide and water.

If we accept Kohlrausch's hypothesis of ionic spheres, it is evident that the atmosphere about the ions remains of the same size throughout all the mixtures; otherwise the ions would tend to show a maximum in conductivity in those mixtures where the atmosphere is smallest, causing a divergence from the fluidity curves. Difference in dissociation would also cause a divergence between the conductivity and fluidity curves. In the above case, however, the dissociation is large and all the curves are parallel.

[1] Ann. der Phys., 52, 328 (1894).

If we pass now to potassium iodide in mixtures of acetone with methyl alcohol and ethyl alcohol, we find, again, that the conductivity curves and fluidity curves are very similar, *i. e.*, nearly straight lines, with a tendency towards a maximum, which is greater in the case of methyl alcohol than in that of ethyl alcohol. Evidently the changes in the size of the ionic spheres and the changes in the dissociation have either counteracted each other or remained zero.

Now let us consider lithium nitrate. In mixtures of acetone with the alcohols, we get a pronounced maximum in conductivity in the 75 per cent mixtures, at high dilutions. Since these solvents gave no such minimum in the case of potassium iodide, the maximum must be connected with the lithium nitrate itself. There are two possible explanations of the phenomenon: (1) Increase in dissociation in the 75 per cent mixture; (2) increase in the mobility of the ions, due to the diminution in the size of the ionic spheres. We shall attempt to decide between these two possibilities.

We have shown by consideration of the fluidities, that the liquids are not more associated in the mixtures than in the pure solvents, hence, if we accept the hypothesis of Dutoit and Aston, that dissociation power increases with the association of the solvent, the maximum cannot be due to increase in dissociation in the mixture. For example, calcium nitrate shows a pronounced maximum in conductivity in mixtures of alcohol and acetone, even though the dissociation of calcium nitrate in pure acetone is very small. It hardly seems probable that the acetone increases the dissociation of pure alcohol if it does not form complexes with it. We also have the fact, found by Jones and Carroll, that even in the case of alcohol and water, where molecular aggregations are known to be formed, there is not an increase in dissociation larger than the possible experimental error. Furthermore, if the 75 per cent mixture has the highest dissociating power, we should not expect to find the maximum migrating from the 25 per cent mixture to beyond the 75 per cent mixture, as the concentration of the dissolved substance decreases. This is the case with lithium nitrate, in mixtures of the alcohols and acetone. Finally, the

maximum in conductivity should manifest itself in the most concentrated solutions of potassium iodide, in mixtures of acetone with the alcohols. This is contrary to the facts. We, therefore, accept, tentatively, the view that *the maximum in conductivity is due, primarily, to a change in the dimensions of the ionic spheres.*

The determination, however, of the dissociation of lithium nitrate in pure alcohol, in pure acetone and in a 75 per cent mixture of these solvents, would be a very important check. Through the kindness of Mr. L. McMaster this point has been tested for acetone and ethyl alcohol, as shown in the table below:

Table XCVII.—Conductivity of Lithium Nitrate in Pure Acetone at 25°.

v.	μ_v 25° corrected.
2000	55.28
2500	62.87
3000	66.42

Table XCVIII.—Conductivity of Lithium Nitrate in a Mixture of 75 Per Cent Acetone and Ethyl Alcohol at 25°.

v.	μ_v 25° corrected.
2000	92.66
2500	100.55
3000	101.88

Table XCIX.—Conductivity of Lithium Nitrate in Pure Acetone at 25°.

v.	μ_v 25° corrected.
2000	37.01
2500	41.04
3000	41.48

The conductivity of the pure acetone used in these experiments was 1.516×10^{-6}; that of the pure alcohol 0.857×10^{-6}.

These results show that complete dissociation is nearly reached only in the pure alcohol, and that the mixture is dissociated about as we might expect from the law of averages. We note that the maximum is very pronounced.

The conclusions of Dutoit and Friderich and of Jones and Carroll, that conductivity is inversely proportional to the viscosity and directly proportional to the association factor of the solvent (or to the amount of dissociation), are incomplete. It fails to take into consideration changes in the dimensions of the ionic spheres.

In the conductivities of lithium nitrate, in mixtures of acetone and water, the decreased fluidity manifests itself again. We notice, however, that the power of the acetone to produce smaller (or more symmetrical) ionic spheres is not destroyed by substituting water for methyl alcohol or ethyl alcohol. Practically all of the dilutions in the 75 per cent mixture of acetone and water show a decided elevation of the conductivity curves above those we should expect from similar measurements with potassium iodide. That increase in dissociation would make itself manifest in this way is doubtful, and our theory is thus strengthened.

Jones and Lindsay's results with lithium nitrate, in mixtures of water and methyl alcohol, do not show this effect, hence the acetone acts peculiarly in this respect. However, acetone behaves exceptionally in other ways.

At this point we should call attention to the fact that lithium forms a very slowly moving ion, *i. e.*, one with a large ionic sphere, while potassium forms a comparatively rapidly moving ion, *i. e.*, one with a small ionic sphere. The anions used do not differ greatly. Calcium forms an ion with a migration velocity between that of lithium and potassium. It was thought best to measure the conductivities of calcium nitrate in all of the mixtures, exactly as with the other salts.

The results show that the tendency towards a maximum in conductivity in the mixtures is very marked indeed. Moreover, they show that calcium nitrate is dissociated in the solvents very differently from lithium nitrate. Calcium nitrate is dissociated to a large extent in water and methyl alcohol, very much less in ethyl alcohol and still less in acetone. In spite of all differences, we are struck by the fact that the maximum *divergence* still tends to manifest itself in the 75 per cent mixture. Especially is this the case with acetone and water.

Let us now turn our attention to the concentrated solutions. In these we find the tendency towards a maximum very small, or entirely absent. If our explanation is correct, then, as the concentration of the salt increases, there will be less of the solvent for the formation of ionic spheres or, in the case of mixtures which tend to reduce the large atmospheres of the dilute solutions, the mass action of the solvent is much diminished.

Calcium nitrate is intermediate in its behavior between potassium iodide and lithium nitrate. It seems reasonable to connect this with the migration velocity. It would be interesting to experiment with sodium, the ion of which has a slow migration velocity, but, as we have shown, sodium iodide, although soluble, is unsuited for this purpose.

Summary.

We have measured the fluidities of mixtures of acetone with methyl alcohol, ethyl alcohol and water and of a few solutions of calcium nitrate in these mixtures.

We have measured the conductivity of various concentrations of lithium nitrate, potassium iodide and calcium nitrate, dissolved in the above mixtures.

These conductivities, in the case of mixtures of acetone and water, exhibit the minimum in conductivity previously observed by several other workers. Moreover, this minimum in conductivity has been shown to be intimately connected with the minimum in fluidity observed in these mixtures, but the conductivity curves of different salts show marked differences.

In the mixtures of acetone and the alcohols, the fluidities are what we should expect from the law of averages, *i. e.*, the fluidity curve is nearly a straight line. From this fact we have concluded that acetone and the alcohols thus far studied do not form more complex molecular aggregations when mixed than were originally present before mixing.

The conductivities of potassium iodide, in mixtures of acetone with methyl alcohol or ethyl alcohol, are also what we should expect from the law of averages—the conductivity curves are nearly straight lines at all dilutions. Again, the

conductivity has been shown to be intimately connected with fluidity.

Lithium nitrate and calcium nitrate, however, give a very pronounced *maximum in conductivity*, in mixtures of acetone with methyl alcohol or ethyl alcohol. Evidently this was an unexpected phenomenon; to explain it all of the factors that could reasonably influence conductivity were collected. After the elimination of several of them, the possible explanations were shown to be either in an increase in dissociation, giving rise to more ions, or in a diminution in the size of the ionic spheres already in the solution.

It was then shown to be possible to eliminate one of these factors by the following considerations:

1. The fluidity of the mixtures of acetone and alcohol shows that there is no increase in molecular aggregation, hence, we should not expect increased dissociation, if we accept the hypothesis of Dutoit and Aston.

2. Jones and Carroll have shown that, even in the case of alcohol and water, there is practically no increase in dissociation in the mixtures.

3. Furthermore, the maximum migrates from the 25 per cent mixture, at high concentration, to the 75 per cent mixture in the more dilute solutions. This would hardly be expected if the dissociating power is greatest in a certain mixture.

4. Potassium iodide shows no tendency towards a maximum of conductivity in the most concentrated solution with which we worked.

5. Very recent measurements, at extreme dilution, have failed to show any great difference in the dissociating power of the mixtures from that of the pure solvents.

We, therefore, seemed justified in the conclusion that the maximum in conductivity is due to a change in the dimensions of the atmospheres about the ions.

The conclusion of Dutoit and Friderich and of Jones and Carroll, that conductivity is proportional to the dissociation, and inversely proportional to the viscosity, has been shown to be incomplete in not taking into consideration possible changes in the size of the ionic spheres.

The conductivities of lithium nitrate and calcium nitrate, in mixtures of acetone and water, again show a tendency towards a maximum, in spite of the great diminution in fluidity.

Finally, it has been pointed out that the tendency to form a maximum in conductivity increases from potassium iodide, through calcium nitrate, to lithium nitrate, which seems to show these effects most strongly. This may be connected with the migration velocities of these ions.

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Contributions from the Sheffield Laboratory of Yale University.

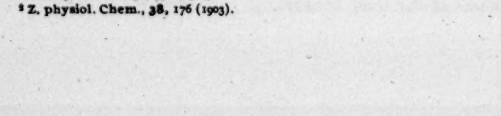
CXXVII.—RESEARCHES ON PYRIMIDINES: ON 2,5-DIAMINO-6-OXYPYRIMIDINE.

[TWELFTH PAPER.]

BY TREAT B. JOHNSON AND CARL O. JOHNS.

In a paper by Wheeler and Johnson[1] on 5-methylcytosine it was stated that work on the preparation of oxydiaminopyrimidines would be carried on in this laboratory. These particular pyrimidine derivatives are of especial interest because of the fact that Kutscher[2] believes he isolated such a compound, in the form of its picrate, from yeast nucleic acid. Kutscher considers that a similar analogy exists between his unknown base and cytosine as exists between thymine and uracil. While thymine differs from uracil by a methyl radical, he thinks that his new base differs from cytosine by an amino group.

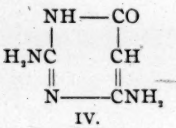
The pyrimidine derivatives that have hitherto been isolated from the decomposition-products of nucleic acid have been mono-oxy or di-oxy derivatives, in which the oxygen atoms occupy position 2 as in cytosine, I., or both positions 2 and 6 as in uracil, II., and thymine, III.:



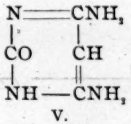
I. II. III.

[1] THIS JOURNAL, 31, 592 (1904).
[2] Z. physiol. Chem., 38, 176 (1903).

It appears to the writers that if Kutscher's base is an oxydiaminopyrimidine, of all the possible diamino derivatives, the most probable forms to be considered are likewise those in which the oxygen atom occupies either position 2 or 6. An examination of the following formulas will show that the only oxydiamino derivatives that fulfil these conditions, assuming that the amino groups are attached to carbon, are: 6-oxy-2,4-diaminopyrimidine, IV., 2-oxy-4,6-diaminopyrimidine, V., 6-oxy-2,5-diaminopyrimidine, VI., and 2-oxy-5,6-diaminopyrimidine, VII.:



IV.



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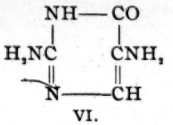
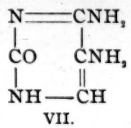


VI.



VII.

Furthermore, since Kutscher obtained his base by hydrolyzing nucleic acid with sulphuric acid, at a high temperature and under pressure, it is evident that the only forms which need to be considered in the above series are those which are capable of undergoing the same treatment without complete decomposition.

Three of the pyrimidines represented above have now been synthesized: 2,4-diamino-6-oxypyrimidine, IV., has been prepared by Traube.[1] He obtained it by condensing guanidine with ethyl cyanacetate in presence of sodium ethylate. That this derivative cannot be the compound obtained by Kutscher is established by the fact that, when it is heated with 20 to 30 per cent sulphuric acid, at 130°–140°, it is completely decomposed.

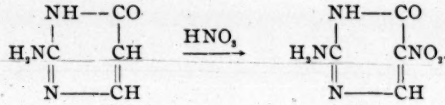
Wheeler and Jamieson[2] have described 2-oxy-4,6-diamino-

[1] Ber. d. chem. Ges., **33**, 1371.

[2] THIS JOURNAL, **32**, 343 (1904).

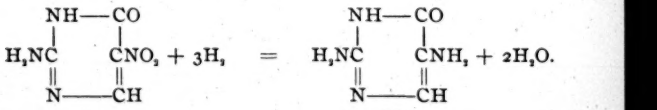
pyrimidine, V. Their experimental evidence excludes the possibility of this pyrimidine being identical with Kutscher's base. It was easily hydrolyzed to barbituric acid when boiled with mineral acids.

In this paper we shall describe the preparation and properties of the diamino derivative represented by Formula VI., *viz.*: 2,5-diamino-6-oxypyrimidine. We have prepared this pyrimidine by three different methods, as follows: When isocytosine[1] was nitrated in the presence of strong sulphuric acid it was converted, practically quantitatively, into 2-amino-5-nitro-6-oxypyrimidine, VIII.:



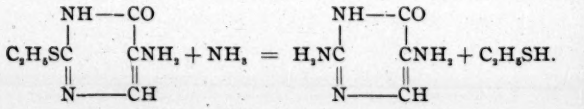
VIII.

When this nitropyrimidine was reduced in an ammoniacal solution with aluminium amalgam, it was converted, smoothly, into 2,5-diamino-6-oxypyrimidine, IX.:



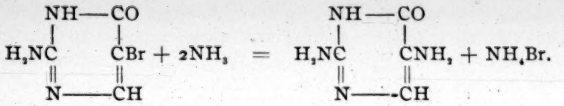
IX.

The same pyrimidine was also formed when 2-ethylmercapto-5-amino-6-oxypyrimidine[2] was heated with alcoholic ammonia.



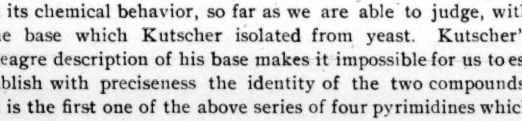
The third method which has served for the preparation of the pyrimidine was by heating bromisocytosine[3] with concentrated, aqueous ammonia.

[1] Wheeler and Johnson: THIS JOURNAL, **29**, 493 (1903).
[2] Johnson: THIS JOURNAL, **34**, 191 (1905).
[3] Wheeler and Johnson: *Loc. cit.*



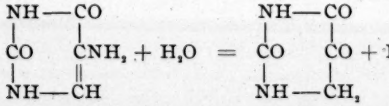
Of the three methods of preparation the first is the only one which is of practical value for the production of the base.

We now find that this 2,5-diamino-6-oxypyrimidine agrees in its chemical behavior, so far as we are able to judge, with the base which Kutscher isolated from yeast. Kutscher's meagre description of his base makes it impossible for us to establish with preciseness the identity of the two compounds. It is the first one of the above series of four pyrimidines which we have been able to heat with sulphuric acid without complete decomposition. Approximately 50 per cent of the pyrimidine was recovered unaltered, after heating with 20 per cent sulphuric acid, at 130°–140°. Part of the base was hydrolyzed by this treatment to a difficultly soluble derivative, which we have identified as 2-amino-5,6-dioxypyrimidine, X. Under the conditions employed in our work we did not observe the formation of aminouracil.



X.

This hydrolysis is perfectly analogous to the formation of oxyuracil, XI., from aminouracil, which was described by Behrend.[1]



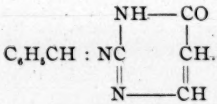
XI.

2,5-Diamino-6-oxypyrimidine crystallizes from water with 1

[1] Ann. Chem. (Liebig), 229, 40.

molecule of water of crystallization. Analogous to Kutscher's base it gives a picrate which is extremely insoluble in water. Notwithstanding its insolubility, it is not a derivative suitable for identifying the base on account of its indefinite decomposition-point and poor crystalline form. The base also forms a beautiful crystalline series of salts with nitric, hydrochloric and sulphuric acids.

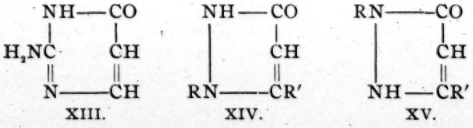
Especially interesting in connection with the nitration of isocytosine was the behavior of its benzal derivative, XII., towards nitric acid:



XII.

While isocytosine nitrates vary easily, to give the 2-amino-5-nitro-6-oxypyrimidine, VIII, its benzal derivative could be recovered unaltered after warming with a mixture of nitric acid (sp. gr. 1.5) and concentrated sulphuric acid, for 24 hours.

On account of their close structural relationship, it might be expected that 2-amino-6-oxypyrimidine, XIII, would show some analogy in its chemical behavior to a 3-pyrazolone, XIV., or a 5-pyrazolone, XV.:



XIII. XIV. XV.

Wheeler and Bristol[1] have shown that when pyrimidine derivatives, having hydrogen both in positions 4 and 5, are attacked by halogens or nitric acid, it is the hydrogen atom in position 5 which is substituted. The 3-pyrazolones[2] and 5-pyrazolones[3] are also readily attacked by halogens, the sub-

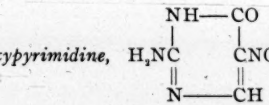
[1] THIS JOURNAL, **33**, 438 (1905).
[2] Ber. d. chem. Ges., **38**, 154.
[3] Knorr and Duden: *Ibid.*, **23**, 766.

stitution taking place in position 4, which corresponds to position 5 in the pyrimidine ring. They also react smoothly, in acetic acid, with sodium nitrite to form characteristic, green-colored nitroso derivatives. We now find isocytosine does not react with nitrous acid ; it was recovered unaltered after remaining in a nitrous acid solution for several hours. We did not observe the formation of any uracil.

Work on the preparation of 2-oxy-5,6-diaminopyrimidine is in progress in this laboratory.

EXPERIMENTAL.

2-Amino-5-nitro-6-oxypyrimidine,



—This nitro derivative was prepared by nitrating isocytosine.[1] After several experiments, in which we used varying proportions of nitric and sulphuric acids, we observed that we obtained the best results when we worked under the following conditions: Six grams of isocytosine were slowly added to a mixture of 18 cc. of nitric acid (sp. gr. 1.5) and 18 cc. of concentrated sulphuric acid. The nitration was very violent and, in order to avoid oxidation, the temperature of the acid mixture was not allowed to rise above 100°. After the final addition of isocytosine the mixture was heated on the steam-bath for 1 hour, to complete the reaction. Longer heating tends to diminish the yield of the nitro product. The acid mixture was thoroughly cooled and poured into 100 cc. of ice-water. The clear yellow solution that resulted was then made slightly alkaline with ammonium hydroxide. On cooling we obtained a beautiful, yellow, crystalline precipitate. It was very difficultly soluble in hot water, from which it separated, on cooling, in clusters of microscopic prisms. It was insoluble in all the ordinary organic media. It was purified for analysis by boiling with glacial acetic acid. It had no definite decomposition point, but began to turn brown at about 280° and did not decompose below 300°. The yield corresponded to 92 per cent

[1] Wheeler and Johnson : *Loc. cit.*

of the theoretical. A nitrogen determination, by Kjeldahl's method, gave:

	Calculated for $C_4H_4O_3N_4$.	Found.
N	35.89	35.70

In order to establish the structure of this nitropyrimidine, it was heated with 20 per cent sulphuric acid, for 4 hours, at 190°–200°. When the solution was examined a beautiful crystalline solid had separated, which had all the properties of nitrouracil. In order to prove that this was nitrouracil it was reduced to aminouracil with aluminium amalgam, in an ammoniacal solution. That aminouracil was the product of the reduction was established by a determination of nitrogen in the free base and by means of its picrate. The picrate showed signs of decomposing at 147° and then decomposed, with violent effervescence, at 245°–247°.[1] A determination of nitrogen in the free base gave the following result:

	Calculated for $C_4H_5O_2N_3$.	Found.
N	33.07	32.99

2,5-Diamino-6-oxypyrimidine, $H_2NC(NH{-}CO)CNH_2.H_2O$.—Five grams of 2-amino-5-nitro-6-oxypyrimidine were suspended in 150 cc. of water, to which 5 cc. of 14 per cent ammonium hydroxide solution had been added. To this ammoniacal solution was then added an excess of aluminium amalgam and the temperature of the solution being kept below 40° during the reduction. The reduction was allowed to proceed for 24 hours, when the aluminium hydroxide was filtered off. We obtained a clear, wine-colored solution, which was concentrated on the steam-bath to about 15 cc. Decomposition took place during this evaporation and a brown, amorphous substance continued to form during prolonged heating. The concentrated solution was filtered and allowed to stand over night. In the morning 1.5 grams of crystalline material had separated. The crystals

[1] Wheeler and Bristol: THIS JOURNAL, **33**, 438 (1905).

were badly etched and were developed in the form of large, radiating prisms. Associated with these prisms was a small amount of amorphous material. Some of the large prisms were removed, washed with cold water and dried in the air. The water of crystallization was determined at 120°–130°.

0.2368 gram substance lost 0.0305 gram.

	Calculated for $C_4H_6ON_4.H_2O$.	Found.
H_2O	12.50	12.88

The anhydrous base had no definite melting-point. It decomposed, with slow effervescence, at about 245°. Analysis (Kjeldahl):

	Calculated for $C_4H_6ON_4$.	Found.
N	44.44	43.96

2,5-diamino-6-oxypyrimidine is extremely soluble in water. When boiled with water the solution assumes a red color and the base apparently slowly oxidizes, with separation of a flocculent, amorphous residue. It is a strong di-acid base and forms a very characteristic series of salts (see below) with nitric, hydrochloric and sulphuric acids. Of these three salts the nitrate and hydrochloride are very soluble in water. The sulphuric acid salt is difficultly soluble in water and is the most characteristic derivative of the base that we have obtained. The base is precipitated by phosphotungstic acid and mercuric chloride. When solutions of platinum chloride and gold chloride were added to an aqueous solution of the base no double salts separated, but the halides were slowly reduced to metallic platinum and gold. With potassiobismuth iodide the base gives a brick-red precipitate.

The *picrate* was formed when picric acid was added to a dilute, aqueous solution of the base. It was very difficultly soluble in water. It separated from hot water in aggregates of short, distorted prisms (Fig. I.). Traces of impurities modify the crystal forms of the salt. Using a pure sample of the base the picrate separated in the form of stout needles. The picrate had no definite decomposition-point, but decomposed at 250°–300°, according to the rate of heating. Analysis:

	Calculated for $C_4H_4NO_4.C_6H_3O_7N_3$.	Found.
N	27.60	27.58

The *dihydrochloride*, $C_4H_6ON_4.2HCl.H_2O$, was prepared by dissolving the base in warm, concentrated hydrochloric acid. When the acid solution was allowed to stand the hydrochloride separated in magnificent, prismatic crystals, some of which measured 5 mm. in length. The prisms showed a decided tendency to twin, as shown in Fig. II. The salt contained 1 molecule of water of crystallization, which was determined by heating at 120°-130°.

0.0896 gram substance lost 0.0077 gram.

	Calculated for $C_4H_6ON_4.2HCl.H_2O$.	Found.
H_2O	8.29	8.59

Analysis of the anhydrous salt:

	Calculated for $C_4H_6ON_4.2HCl$.	Found.
N	28.14	28.07

The *nitrate*, $C_4H_6ON_4.2HNO_3$, was obtained by dissolving the base in 20 per cent nitric acid and allowing it to evaporate in a vacuum. It crystallized in beautiful prisms, which were well developed, with very distinct faces (Fig. III.). They were exceedingly soluble in water. The salt did not contain water of crystallization. Analysis:

	Calculated for $C_4H_6ON_4.2HNO_3$.	Found.
N	33.3	33.5

The *sulphate*, $C_4H_6ON_4.H_2SO_4$, was easily obtained when dilute sulphuric acid was added to an aqueous solution of the base. It was very difficultly soluble in water and separated in the form of slender, needle-like prisms. The salt showed a tendency to crystallize in two forms. When deposited from water it usually separated in clusters of radiating needles. When recrystallized from dilute sulphuric acid solution it formed beautiful, long, slender prisms with well-developed faces (Fig. IV.). Neither form contains water of crystallization. Both forms represent the same salt. The salt does not decompose below 300°.

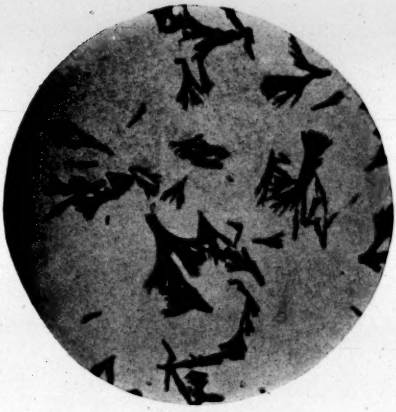


Fig. I.—The picrate of 2,5-diamino-6-oxypyrimidine crystallized from water. Magnified 60 times.

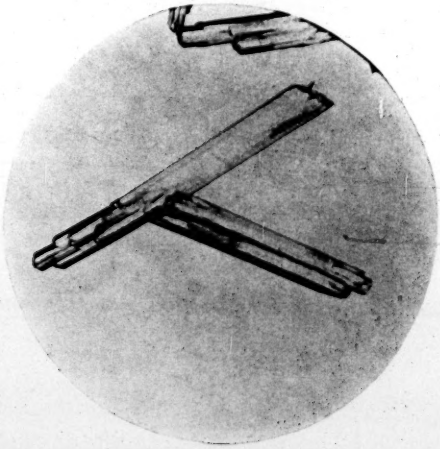


Fig II.—The hydrochloride of 2,5-diamino-6-oxypyrimidine crystallized from a strong solution of hydrochloric acid. Magnified 60 times.

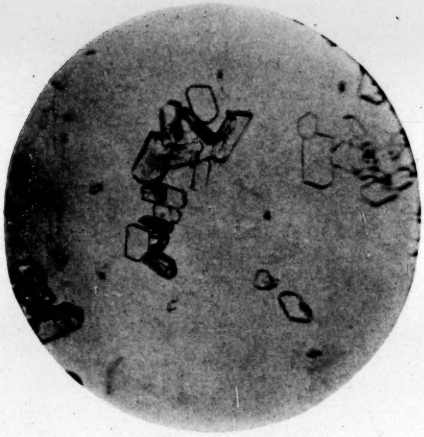


Fig. III.—The nitrate of 2,5-diamino 6-oxypyrimidine crystallized from a strong nitric acid solution. Magnified 60 times.

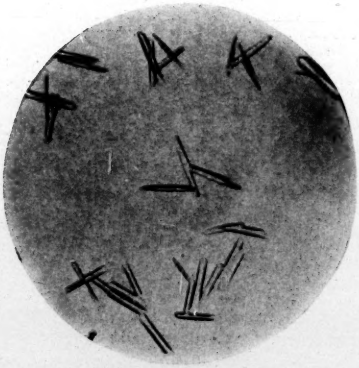


Fig. IV.—The sulphate of 2,5-diamino-6-oxypyrimidine crystallized from dilute sulphuric acid. Magnified 60 times.

Analysis of the needles and prisms of the salt :

	Calculated for $C_4H_6ON_4.H_2SO_4$.	Found. I.	II.
N	25.00	24.81	24.74

In order to avoid the possibility of dissociation in aqueous solution, solubility determinations of the sulphate were made in normal solutions of sulphuric acid. The solubility was determined by taking exactly 10 cc. of the acid solution, saturated at 25°, and determining the amount of nitrogen present (Kjeldahl). The quantity of salt dissolved in 10 cc. was then calculated from the weight of nitrogen obtained. One hundred cc. of normal sulphuric acid dissolved, at 25° :

I.	II.
0.4928 gram.	0.4704 gram.

While the 2,5-diamino-6-oxypyrimidine apparently undergoes slow decomposition when its aqueous solution is boiled, the sulphate appears to be perfectly stable when subjected to the same treatment. Some of the sulphate was dissolved in 20 per cent sulphuric acid and the solution boiled for about one-half hour. The sulphuric acid was then removed by digesting with pulverized barium carbonate. After filtering from barium carbonate and barium sulphate the filtrate was combined with a solution of picric acid. The picrate that was obtained agreed in all its properties with the picrate of 2,5-diamino-6-oxypyrimidine. Analysis :

	Calculated for $C_4H_6ON_4.C_6H_3O_7N_3$.	Found.
N	27.60	27.66

Behavior of 2,5-Diamino-6-oxypyrimidine when Heated with Sulphuric Acid under Pressure.—This experiment was of especial interest since Kutscher[1] obtained his base by hydrolyzing nucleic acid with sulphuric acid, at a high temperature and under pressure. One gram of the sulphuric acid salt of the pyrimidine base was heated in a sealed tube, with 10 cc. of sulphuric acid, of approximately 20 per cent, for 3 hours, at 130°–140°. There was no pressure when the tube was opened and no apparent decomposition had taken place. The sul-

[1] *Loc. cit.*

phuric acid was removed by digesting with pulverized barium carbonate and, after filtering from barium carbonate and barium sulphate, the filtrate was evaporated over a free flame to about 50 cc. Some of this solution was taken and treated with a cold, saturated solution of picric acid. We obtained an immediate precipitate of a beautiful, crystalline picrate. It was extremely insoluble in water. It separated from hot water in well-developed prisms, which arranged themselves in radiating clusters. The picrate had all the properties of the picrate of 2,5-diamino-6-oxypyrimidine. Analysis (Kjeldahl):

	Calculated for $C_4H_8ON_4.C_6H_3O_7N_3$.	Found.
N	27.60	27.53

The remaining portion of the above filtrate, after testing for unaltered base with picric acid, was allowed to stand for 2 days, when a small amount of crystalline material separated. It was purified by recrystallizing from water, from which it separated in clusters of microscopic prisms. When heated in a capillary tube the material turned brown, but did not decompose below 300°. A nitrogen determination agreed very closely with the calculated for aminouracil or its isomer, *2-amino-5,6-dioxypyrimidine*. The low result obtained was due to the presence of a minute trace of inorganic material ($BaCO_3$?).

	Calculated for $C_4H_5O_2N_3$.	Found.
N	33.0	32.4

In order to distinguish between aminouracil and 2-amino-5,6-dioxypyrimidine, the base was dissolved in hot water and treated with a saturated solution of picric acid. The picrate separated in the form of microscopic prisms. It showed no signs of decomposing at 147°. It charred at 240°–250°, but did not effervesce below 280°. Aminouracil decomposes at 247° with violent effervescence.[1]

Action of Ammonia on Bromisocytosine or 2-Amino-5-brom-6-oxypyrimidine.—Three grams of bromisocytosine[2] were heated

[1] Wheeler and Bristol: *Loc. cit.*

[2] Wheeler and Johnson: *Loc. cit.*

with an excess of aqueous ammonia, for 6 hours, at 190°–215°. When the tube was opened the solution was perfectly clear and no resin had separated. The solution gave a heavy precipitate of silver bromide when treated with nitric acid and silver nitrate. The ammoniacal solution was evaporated over a free flame to remove the excess of ammonia. On continued evaporation the solution gradually assumed a deep wine color and a slimy deposit slowly formed on the surface of the liquid. After the excess of ammonia was removed the solution was filtered and combined with a solution of picric acid, which yielded a very insoluble picrate. It was poorly crystallized and showed no definite decomposition-point. It gave no test for bromine. A nitrogen determination agreed with that calculated for the picrate of 2,5-diamino-6-oxypyrimidine.

	Calculated for $C_4H_6NO_4.C_6H_3O_7N_3$.	Found.
N	27.60	28.10

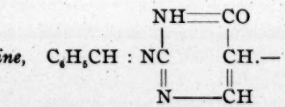
Action of Ammonia on 2-Ethylmercapto-5-amino-6-oxypyrimidine.[1]—When 2-ethylmercapto-5-amino-6-oxypyrimidine was heated in a sealed tube, with an excess of concentrated aqueous ammonia, at 131°–142°, for 4 hours it was recovered unaltered. It was again heated for 3 hours, at 180°–190°. Under these conditions only a trace of mercaptan was detected and again unaltered material was obtained. Three grams of the mercapto derivative were then heated for 4 hours, at 200°–205°, with strong alcoholic ammonia. When the tube was opened there was slight pressure and a strong odor of mercaptan. A small amount of slimy, insoluble residue had also separated. The solution was filtered and evaporated to dryness. We obtained a red-colored oil, which showed no signs of solidifying. It was dissolved in water and boiled with animal charcoal to remove the color. When the clarified solution was treated with picric acid we obtained a picrate which was difficultly soluble in water. It gave no test for sulphur and decomposed at 250°–300°, according to the rate of heating. A nitrogen determination agreed with the calculated for the picrate of 2,5-diamino-6-oxypyrimidine.

[1] Johnson : *Loc. cit.*

	Calculated for $C_4H_6ON_4.C_4H_8O_7N_2$.	Found.
N	27.60	27.71

Hydrochloric Acid Salt of 2-Amino-5-benzoylamino-6-oxypyrimidine, .HCl.—An aqueous solution of guanidine was prepared by dissolving 25 grams of guanidine carbonate in water and then adding an aqueous solution containing a molecular proportion of barium hydroxide. The barium carbonate was filtered off and to the solution was added 50 grams of the sodium salt of ethyl formylhippurate. The solution was then heated on the steam-bath for 1–2 hours. The clear liquid was made distinctly acid with sulphuric acid and concentrated to about one-half its volume. Upon cooling, nothing separated. The solution was now treated with a slight excess of mercuric chloride, when a white mercury salt was obtained. This was washed with water and decomposed with hydrogen sulphide. On evaporating the filtrate, after filtering from mercuric sulphide and cooling, a crystalline product was obtained. It was insoluble in alcohol, but crystallized from hot water in microscopic needles. It contained chlorine and decomposed with violent effervescence at about 275°. We did not obtain a sufficient amount of the salt to isolate the free base. Analysis (Kjeldahl) :

	Calculated for $C_{11}H_{11}O_2N_4Cl$.	Found.
N	21.01	21.04

2-Benzalamino-6-oxypyrimidine,  —Five grams of isocytosine were heated at 160°–180°, for 3 hours, with a molecular proportion of benzaldehyde. Water was given off and a yellow, crystalline cake was obtained. It

was insoluble in water and alcohol. It showed both acid and weak basic properties. It dissolved in ammonia to a deep red solution. Its salts undergo dissociation in aqueous solution. Some of the material was dissolved in 20 per cent sulphuric acid and filtered while hot into cold water. The base was precipitated at once as a yellow, crystalline solid. After washing with water and alcohol, it decomposed at 238°-242°. Analysis:

	Calculated for $C_{11}H_9ON_3$.	Found.
N	21.10	21.11

The following experiments illustrate the remarkable stability of this pyrimidine towards nitric acid: Eight and one-half grams of the crude material were dissolved in a mixture of 20 cc. of nitric acid (sp. gr. 1.5) and 15 cc. of concentrated sulphuric acid. The mixture was warmed on the steam-bath for 3 hours and then allowed to stand for 24 hours at 40°-60°. We obtained a clear, red solution. When the acid solution was poured into water a crystalline product separated which was identified as a mixture of the unaltered benzal derivative and some metanitrobenzaldehyde. After boiling with alcohol, to remove the nitrobenzaldehyde, the benzalaminopyrimidine was obtained, melting at about 242°. When mixed with the pure material the melting-point was not altered. When the benzal derivative was again heated with a mixture of nitric acid (sp. gr. 1.5) and concentrated sulphuric acid, at 90°-100°, no nitro-product was obtained but a violent oxidation took place and the pyrimidine was completely decomposed.

Action of Nitrous Acid on Isocytosine.—Four grams of isocytosine were dissolved in acetic acid. Into this solution was introduced solid sodium nitrite and the liquid allowed to stand over night, at the ordinary temperature. In the morning a crop of microscopic prisms had separated. When fused on platinum foil they left no inorganic residue. The material was very soluble in cold water. It turned brown at about 280°, but did not melt at 300°. A nitrogen determination agreed with that calculated for an acetic acid salt of isocytosine.

	Calculated for $C_6H_5O_2N_3$.	Found.
N	24.56	24.26

NEW HAVEN, CONN.,
June 7, 1905.

THE REACTION BETWEEN ORGANIC MAGNESIUM COMPOUNDS AND UNSATURATED COMPOUNDS.

VII. COMPLEX PRODUCTS FROM CINNAMIC ESTERS.

BY E. P. KOHLER AND GERTRUDE HERITAGE.

It has frequently been pointed out in these papers[1] that the reaction between Grignard's reagent and unsaturated esters may lead to complex products derived from 2 molecules of the unsaturated compound. As a rule, a number of these dimolecular products are formed at the same time, hence it is exceedingly difficult to isolate pure substances from the resulting mixtures. In the case of cinnamic esters, however, we have succeeded in separating a sufficient number to show the general course of the reaction.

In anticipation of experimental difficulties, we decided to begin with the phenyl ester, because phenol is easily estimated quantitatively and it is possible, therefore, to determine the amount of phenoxyl in the product. As no experiments on Grignard's reagent and phenyl esters have been described, we made a preliminary study of the action of phenylmagnesium bromide on phenyl phenylcinnamate—an ester with which no complications were to be expected. The results—published in the first part of this paper—show that phenyl esters of unsaturated acids react essentially like alkyl esters. In accordance with this we found that, when phenyl cinnamate is added to excess of carefully cooled, ethereal phenylmagnesium bromide, the two products are magnesium derivatives of phenyl diphenylpropionate and diphenylpropiophenone:

$$C_6H_5CH : CHCO_2C_6H_5 + C_6H_5MgBr =$$

$$(C_6H_5)_2CHCH : C\begin{matrix}OMgBr\\ OC_6H_5\end{matrix};$$

[1] This JOURNAL, 31, 643; 33, 21, 35, 153, 333; 34, 132.

$$C_6H_5CH : CHCO_2C_6H_5 + 2C_6H_5MgBr = (C_6H_5)_2CHCH : C\begin{matrix}OMgBr\\ C_6H_5\end{matrix} + Mg(OC_6H_5)Br.$$

These are, therefore, the substances which subsequently form complex products by reacting with additional ester.

On reversing the procedure—adding ethereal phenylmagnesium bromide to excess of carefully cooled ester—we obtained a substance whose analysis and molecular weight correspond to the formula $C_{36}H_{30}O_3$. It will be shown, in the experimental part, that this is a β-ketonic ester, whose structure is represented by the formula

$$(C_6H_5)_2CHCHCOCH_2CH(C_6H_5)_2.$$
$$\quad\quad\quad

II. $(C_6H_5)_2CHCHCOCH : CHC_6H_5 + C_6H_5MgBr =$
$\quad\quad\quad

but turns brown at higher temperatures and ultimately chars below its boiling-point, under 20 mm. pressure. The ester was, therefore, made from the crude chloride, which contained variable quantities of chlorides of phosphorus. The chloride was mixed with a considerable excess of phenol and the mixture heated on a steam-bath until there was no further evolution of hydrochloric acid. On pouring the resulting pale-yellow liquid into hot alcohol, the ester separated in stout needles These were filtered, washed thoroughly with cold alcohol and purified by recrystallization from a mixture of alcohol and chloroform.

0.2323 gram substance gave 0.7154 gram CO_2 and 0.1146 gram H_2O.

	Calculated for $C_{21}H_{16}O_2$.	Found.
C	84.00	83.99
H	5.33	5.48

The ester melts at 142°. It is very sparingly soluble in alcohol and ether, moderately in acetone and benzene, readily in chloroform.

It is interesting to note that, while methyl phenylcinnamate reacts only with 1 molecule of phenylmagnesium bromide, the corresponding phenyl ester invariably reacts with two.

Triphenylpropiophenone, $(C_6H_5)_2CHCHCOC_6H_5$ (with C_6H_5 on the CH).—A benzene solution of phenyl phenylcinnamate was added to excess of ethereal phenylmagnesium bromide, the mixture boiled for a short time and treated in the usual way. The product was purified by solution in chloroform and precipitation with hot, absolute alcohol. It was obtained in small, colorless needles, melting at 182°. Analysis:

I. 0.1376 gram substance gave 0.4520 gram CO_2 and 0.0747 gram H_2O.

II. 0.1272 gram substance gave 0.4170 gram CO_2 and 0.0686 gram H_2O.

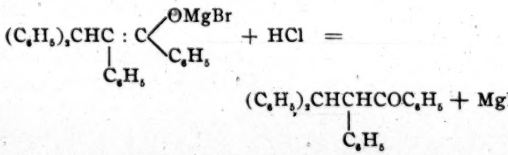
	Calculated for $C_{27}H_{22}O$.	Found. I.	II.
C	89.50	89.66	89.41
H	6.08	6.03	6.00

Molecular Weight in Boiling Acetone.

K = 1710.

Solvent. Grams.	Substance. Grams.	Elevation of boiling-point.	Molecular weight.
59.6	0.691	0.055	370
"	1.415	0.120	350
"	1.954	0.161	348
	Calculated for $C_{27}H_{22}O$,		362

The ketone is readily soluble in chloroform, moderately in benzene and boiling acetone, very slightly in alcohol and ether. Like benzpinakolin, and other ketones in which the carbonyl is surrounded by a number of complex groups, it forms neither hydrazone nor oxime. A similar "steric" effect is seen in the lack of reactivity of the magnesium derivative of the ketone, for while other magnesium derivatives readily react with halogens and with acid chlorides, that of this ketone does not react with any of these substances and reacts but slowly with such as replace magnesium with hydrogen:



II. Phenyl Cinnamate and Phenylmagnesium Bromide.

In order to get the primary products of the reaction the substances were first brought together at the lowest temperature available. A dilute, ethereal solution of the ester (22.4 grams, 1 mol.) was added, very slowly, to an ethereal solution of phenylmagnesium bromide (3 mols.) that was cooled in a mixture of ice and ammonium chloride. The product was immediately decomposed with iced hydrochloric acid. After evaporating the ether, the residue was boiled for an hour with alco-

holic potassium hydroxide. The result was 11.1 grams of diphenylpropionic acid, 12.6 grams of diphenylpropiophenone and a small quantity of diphenyl.

The experiment was repeated under exactly the same conditions, but the solution of the bromide (1 mol.) was slowly siphoned into a cooled solution of the ester (2 mol.). No solid products were obtained. The ethereal layer, on evaporation, left an oil that contained a considerable quantity of unchanged ester. This was removed by hydrolysis with alcoholic potassium hydroxide, at the ordinary temperature. After removing the potassium salts with water there remained a yellow oil which was unsaturated and which, in acetone solution, readily reduced potassium permanganate. The oxidation-products were: diphenylpropionic acid, benzoic acid and carbon dioxide. From these results we conclude that the oil consisted, mainly, of triphenylpentanone,

$$(C_6H_5)_2CHCH_2COCH : CHC_6H_5.$$

More definite results were obtained when the experiment was repeated with equimolecular amounts of the reagents. The mixture was allowed to stand over night, at the ordinary temperature and then treated in the usual way. The ethereal layer slowly deposited a crystalline solid, which was filtered, thoroughly washed with absolute alcohol and repeatedly recrystallized from a mixture of chloroform and absolute alcohol. The substance was thus obtained in long needles, melting at 180°–182°. It is readily soluble in chloroform and benzene, moderately in ethyl acetate and boiling acetone, very slightly in alcohol and ether. Analysis:

I. 0.1615 gram substance gave 0.5008 gram CO_2 and 0.0838 gram H_2O.

II. 0.1284 gram substance gave 0.3987 gram CO_2 and 0.0680 gram H_2O.

	Calculated for $C_{24}H_{20}O_3$.	Found. I.	Found. II.
C	84.70	84.57	84.49
H	5.88	5.76	5.88

Molecular Weight in Boiling Chloroform.

K = 39.5.[1]

Solvent. Grams.	Substance. Grams.	Elevation of boiling-point.	Molecular weight.
100.2	0.907	0.080	446
"	1.850	0.162	446
	Calculated for $C_{36}H_{30}O_3$,		510

The substance is very easily hydrolyzed. An alcoholic solution containing 4.682 grams substance was boiled, for an hour, with excess of potassium hydroxide, the alcohol distilled, the residue diluted with water and extracted with ether. The aqueous solution contained potassium phenolate and potassium carbonate, but no salt of an organic acid. It was diluted to a known volume and the phenol determined in the usual way. The result was 2.918 grams of tribromphenol, instead of 3.047 grams calculated for $C_{29}H_{35}O.CO_2C_6H_3$. The substance is, therefore, the phenol ester of a monobasic acid that loses carbon dioxide during the process of hydrolysis.

The ethereal solution, on evaporation, left 3.395 grams of a solid that was purified by recrystallization from absolute alcohol. It was deposited in colorless needles, melting at 130°. It is moderately soluble in alcohol and acetone, readily in ethyl acetate and chloroform. Analysis:

I. 0.1430 gram substance gave 0.4700 gram CO_2 and 0.0845 gram H_2O.

II. 0.1324 gram substance gave 0.4323 gram CO_2 and 0.0775 gram H_2O.

	Calculated for $C_{22}H_{26}O$.	Found. I.	Found. II.
C	89.03	89.64	89.02
H	6.66	6.56	6.44

Molecular Weight in Boiling Acetone.

K = 1710.

Solvent. Grams.	Substance. Grams.	Elevation of boiling-point.	Molecular weight.
52.70	0.8540	0.127	357
"	1.3975	0.226	350
	Calculated for $C_{29}H_{26}O$,		390

[1] This value was obtained by experiment with the chloroform used.

These results show that the hydrolysis is represented by the equation

$$C_{29}H_{28}O.CO_2C_6H_5 + H_2O = C_{29}H_{26}O + C_6H_5OH + CO_2.$$

The new compound is a saturated ketone; it does not combine with bromine, it is not attacked by potassium permanganate and it forms an oxime. An alcoholic solution containing 1 molecule of the substance, 3 molecules of hydroxylamine hydrochloride and 9 molecules of potassium hydroxide was boiled for several hours, then poured into ice-water. The oxime separated as a granular solid, which was purified by crystallization from alcohol. Analysis:

I. 0.2071 gram substance gave 0.6514 gram CO_2 and 0.1274 gram H_2O.

II. 0.1905 gram substance gave 0.6113 gram CO_2 and 0.1163 gram H_2O.

	Calculated for $C_{29}H_{27}ON$.	Found. I.	II.
C	85.92	85.78	86.03
H	6.66	6.83	6.69

The oxime is readily soluble in alcohol and ether, insoluble in water. From alcohol it separates in needles, melting at 115°–116°. For the purpose of rearrangement by Beckmann's reaction it was dissolved in absolute ether and treated with a slight excess of phosphorus pentachloride. The substances reacted vigorously at the ordinary temperature. The ether was removed by distillation and the horny residue boiled with water until it was completely transformed into a hard, granular solid. This was purified by repeated recrystallization from absolute alcohol. It was thus obtained in small, lustrous prisms, melting at 155°. Analysis:

0.2590 gram substance gave 0.8142 gram CO_2 and 0.1600 gram H_2O.

	Calculated for $C_{29}H_{27}ON$.	Found.
C	85.92	85.75
H	6.66	6.80

The analytical results showed that the compound is isomeric

with the oxime and therefore, probably, a substituted acid anilide. This conclusion was easily verified by heating the substance with concentrated hydrochloric acid, for 8 hours, at 160°. There was no pressure on opening the tube. The contents were diluted with water and extracted with ether. The ethereal solution contained only β,β-diphenylpropionic acid, which was identified by comparison with a specimen from another source.

The aqueous solution was evaporated to complete dryness and the residue recrystallized from a small quantity of water. It separated in colorless needles, melting at 253°. This corresponds, fairly closely, to the melting-point (255°) of diphenylethylamine hydrochloride. From an aqueous solution of the salt potassium hydroxide liberated a liquid base, whose composition was determined by analysis of its platinochloride.

0.1495 gram salt gave 0.3685 gram Pt.

	Calculated for $C_{28}H_{30}N_2Cl_6Pt$.	Found.
Pt	24.25	24.56

These products—β,β-diphenylpropionic acid and β,β-diphenylethylamine—show that the ketone, $C_{29}H_{26}O$, is tetraphenylpentanone, the successive steps in the transformation being represented by the following equations:

I. $[(C_6H_5)_2CHCH_2]_2CO + NH_2OH = [(C_6H_5)_2CHCH_2]_2CNOH + H_2O$;

II. $(C_6H_5)_2CHCH_2\overset{\overset{NOH}{|}}{C}CH_2CH(C_6H_5)_2 \rightarrow (C_6H_5)_2CHCH_2CONHCH_2CH(C_6H_5)_2$;

III. $(C_6H_5)_2CHCH_2CONHCH_2CH(C_6H_5)_2 + H_2O = (C_6H_5)_2CHCH_2CO_2H + (C_6H_5)_2CHCH_2NH_2$.

Since tetraphenylpentanone is symmetrical, there are but two possible formulas for the original product, $C_{36}H_{30}O_3$, *viz.*:

$$(C_6H_5)_2\overset{\overset{CO_2C_6H_5}{|}}{C}CH_2COCH_2CH(C_6H_5)_2,$$

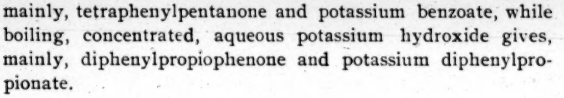
or $(C_6H_5)_2CHCHCOCH_2CH(C_6H_5)_2$.
$\quad\quad\quad

	Calculated for $C_{21}H_{22}O_3$.	Found. I.	II.
C	83.04	83.10	82.90
H	6.25	6.22	6.30

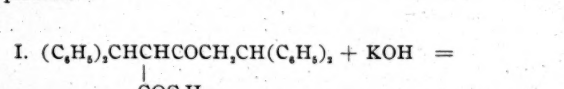
When heated to 200°, with concentrated hydrochloric acid, the substance breaks down into 2 molecules of diphenylpropionic acid:

$$(C_6H_5)_2CHCHCOCH_2CH(C_6H_5)_2 + 2H_2O =$$
$$\quad\quad\quad

The structure of the ketone follows from the products of hydrolysis. Boiling alcoholic potassium hydroxide gives, mainly, tetraphenylpentanone and potassium benzoate, while boiling, concentrated, aqueous potassium hydroxide gives, mainly, diphenylpropiophenone and potassium diphenylpropionate.



I. $(C_6H_5)_2CHCHCOCH_2CH(C_6H_5)_2 + KOH =$
COC_6H_5
$[(C_6H_5)_2CHCH_2]_2CO + C_6H_5CO_2K$;



II. $(C_6H_5)_2CHCHCOCH_2CH(C_6H_5)_2 + KOH =$
COC_6H_5
$(C_6H_5)_2CHCH_2COC_6H_5 + (C_6H_5)_2CHCH_2CO_2K.$

Both reactions take place when the ketone is heated, at 180°, with concentrated hydrochloric acid.

A still more complex substance was obtained whenever ethereal solutions containing ester and reagent were boiled for 3 or 4 hours, before treatment with ice-water. The products, under these conditions, consist largely of oils that do not solidify, but by cautious addition of acetone and alcohol it is generally possible to get a small quantity of solid. By crystallization from chloroform this can be separated into the ketone described above and a substance which melts at 153°. It is readily soluble in acetone and chloroform, moderately in alcohol. Analysis:

I. 0.2102 gram substance gave 0.6468 gram CO_2 and 0.1129 gram H_2O.

II. 0.2358 gram substance gave 0.7582 gram CO_2 and 0.1354 gram H_2O.

	Calculated for $C_{40}H_{36}O_2$.	Found. I.	II.
C	88.11	87.67	87.70
H	6.28	6.23	6.37

Molecular Weight Determined in Boiling Acetone.

Solvent. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
79.68	1.1888	0.042	604
"	2.2628	0.080	605
	Calculated for $C_{42}H_{36}O$,		572

The composition and molecular weight of this compound correspond to those of the tertiary alcohol that would be obtained by the action of phenylmagnesium bromide on the ketone described above, namely :

$$(C_6H_5)_2CHCHCOCH_2CH(C_6H_5)_2.$$
$$\quad\quad\quad

Contributions from the Chemical Laboratory of the University of Cincinnati.

LXVII.—THE USE OF POTASSIUM PERIODATE IN THE DETECTION OF MANGANESE, COBALT AND ZINC.

By Stanley R. Benedict.

Potassium periodate[1] has received few, if any, applications to qualitative analysis. There are, however, reactions obtainable with this reagent which afford very delicate, reliable and rapid methods for the detection of certain metals.

Among these is manganese. Since very satisfactory tests are already known for this element, *viz.*, formation of manganate and permanganate, the proposal of a new test for manganese would be justified only by its possession of exceptional advantages. It is believed that the test to be described possesses such advantages in the matter of time consumed and ease of manipulation, while it is by no means lacking in delicacy or in reliability.

If a solution of a manganous salt be treated with a solution of potassium periodate, a deep-red precipitate forms at once, except in very dilute solutions. In these a red coloration makes its appearance. So far as I am able to learn from literature available, this reaction between manganous salts and periodate has never been subjected to any investigation whatever. I can find no mention of the reaction nor any description of a manganese periodate in articles dealing with periodates.

I have, as yet, had time to make only a superficial examination of a few of the properties of the red precipitate obtained from manganous salts and periodate. It dissolves quite readily in hydrochloric acid, liberating some chlorine. In contact with sodium hydroxide the red precipitate changes, practically instantly, to a black substance which is, apparently, a hydrated manganese dioxide. Ammonium hydroxide produces the same change, which, in this case, goes on more slowly.

[1] The potassium periodate referred to in this article is Kahlbaum's "potassium periodate." I have not yet determined its formula. KIO_4 is the one usually ascribed to it.

The precipitate gives the reaction for periodate which is mentioned later and, from the slight examination given it, appears to be a manganous periodate, although in color it closely resembles manganic salts, and it would seem possible that it might be a manganic iodate or periodate, a portion of the reagent serving as an oxidizing agent.

The formation of the red precipitate or coloration upon addition of periodate to a manganous solution serves as a convenient and delicate test for manganese. The reagent used is N/10 potassium periodate. The addition of 1 or 2 drops of this solution to neutral or ammoniacal solutions of manganese, produces at once a red precipitate, or, if the amount of manganese present be very small, a red coloration. If the solution be neutral the precipitate retains its color, whereas, if it be ammoniacal, the color changes quite rapidly to brown or black. The characteristic color of the manganese periodate makes its appearance in solutions as dilute as a N/10,000 manganous chloride. This is also about the limit of the red lead-nitric acid test for manganese, the depth of color obtained with the two tests being very much the same. The periodate test is slightly more delicate in neutral than in ammoniacal solutions if both solutions are cold, but in warm ammoniacal solution the test is of about equal delicacy with that in neutral solution. Warming of the ammoniacal solution is not necessary except in testing for the merest traces of manganese.

Zinc does not interfere with the periodate test for manganese. In fact periodate constitutes an excellent reagent for detecting both zinc and manganese in one solution. Pure solutions of zinc salts yield a white precipitate with periodate. If, however, ammonium chloride and ammonium hydroxide be present, this precipitation is entirely prevented in the cold unless there is a large amount of zinc, in which case a portion will be precipitated. If the solution is now filtered and the filtrate heated to boiling, the rest of the zinc is completely precipitated. The method for the detection of both elements is as follows: The sulphides are dissolved in very dilute hydrochloric acid and the solution boiled to expel hydrogen sulphide, some

ammonium chloride is added and the solution made strongly ammoniacal. A few cubic centimeters of N/10 potassium periodate are now added. If a pink or red precipitate appears manganese is present. This precipitate will usually soon become brown or black in color. The solution is now filtered and a few drops of periodate added to the filtrate, to insure a slight excess of the reagent. The filtrate is then heated to boiling. Formation of a precipitate, white but colored pink by the solution if manganese was present, indicates zinc. If a white precipitate formed first upon addition of the periodate, manganese was absent and zinc present in large amount. The solution should then be filtered, a little more periodate added and the liquid heated to boiling; a white precipitate confirms zinc.

The following method for the qualitative detection and separation of manganese and zinc is proposed as requiring less periodate than does the one given above. The solution is treated with ammonium chloride and ammonium hydroxide as before. One drop of potassium periodate is added to a small portion of the solution; a pink or red coloration indicates manganese. If manganese is present, sodium phosphate is now added in slight excess to the main portion of the solution. This completely precipitates manganese, in presence of ammonium salts, without precipitating zinc. The solution is filtered and zinc detected in the filtrate by either periodate (with heating), ferrocyanide, or hydrogen sulphide.

Before leaving the subject of the reaction of manganous salts with periodate, it may be well to mention that I have frequently used manganese as a reagent for detecting periodate in presence of iodate, iodide, etc. Iodate gives neither coloration nor precipitation with manganese in presence of ammonium chloride and ammonium hydroxide, so that periodate can readily be detected, in the presence of iodate and other substances which interfere with many tests, by addition of a few drops of the solution to a solution of manganese chloride, to which has been added ammonium chloride and ammonium hydroxide. Red coloration or precipitation shows periodate. This reaction is delicate and characteristic for periodate.

In the presence of excess of nickel, the detection of cobalt is

a matter of some difficulty. Vogel's[1] method, requiring the use of ammonium thiocyanate, amyl alcohol and ether, is too well known to need description here. It is probably the most delicate so far proposed and will detect 0.5 per cent of cobalt in nickel solutions. In a previous paper[2] the author described a method for the detection of both nickel and cobalt by means of sodium hydroxide solution. The method there described detects 1 per cent of cobalt in nickel solutions, the procedure being considerably simpler than in Vogel's process.

If potassium periodate be used as reagent, it is possible to detect as small an amount as 0.1 per cent of cobalt in nickel solutions. The procedure consists only in the addition of the reagent, and, if the quantity of cobalt be under 1 per cent, heating the mixture to boiling.

Addition of potassium periodate to pure nickel solutions gives a light-green precipitate, which changes only slightly upon boiling, losing some of its greenish tint and becoming faintly gray in color.

Potassium periodate added to cobalt solutions gives, at first, a dark-brown precipitate. Upon further addition of the reagent, this precipitate becomes greenish in color and finally dissolves upon heating, forming a greenish-black solution.

It is upon the difference in color of the precipitates given by nickel and cobalt solutions with periodate, and the fact that the color of the cobalt precipitate makes itself apparent upon boiling, even if the amount present be very small, that the following test for cobalt depends.

To about 2–3 cc. of the solution, best N/2 to 2 N in strength, about 1 cc. of N/10 potassium periodate is added and the color of the precipitate thus obtained is observed. If it is light-green, cobalt is either entirely absent or is present in quantity under 1 per cent. The solution is now heated to boiling. If cobalt is absent the precipitate will change only very slightly, becoming somewhat lighter in color and losing some of its greenish tint. If, however, cobalt is present the precipitate will become more or less olive-green, the depth of color being

[1] Ber. d. chem. Ges., **12**, 2314 (1879).
[2] J. Am. Chem. Soc., **26**, 695 (1904).

dependent upon the amount of cobalt present. Where it is desired to detect very small amounts of cobalt, *i. e.*, under 0.5 per cent, it is desirable to have a check-tube containing pure nickel solution of about the same concentration as the test solution. Add periodate to both, heat to boiling and compare for one-half minute. If a greater depth of color is apparent in the test solution than in the blank, cobalt is present. If cobalt was originally present in quantity over 1 per cent, the precipitate will show a brownish- or olive-green tint in the cold, the depth of color being dependent upon the amount of cobalt present.

This test is very reliable and, as stated above, will detect 0.1 per cent of cobalt in nickel solutions, which is considerably less than can be detected by any other method of which I have been able to find record. Other metals than nickel and cobalt should be absent, although zinc will not interfere unless present in large amount. The solution in which the test is made should be neutral. If the precipitate turns black, either in the cold or upon boiling, manganese is present in small amount. Since this black coloration appears with the merest traces of manganese, which element is often found as impurity in nickel salts, the test becomes valuable for ascertaining the general freedom of nickel salts from manganese and cobalt.

REPORT.

Radiothorium—A New Radioactive Element.

Sir William Ramsay has recently[1] discovered a new radioactive element and has thus added another to his long list of epoch-making contributions to inorganic chemistry. This new element was found in a mineral from the island of Ceylon, called "Thorianite." Ramsay became interested in the mineral on account of the comparatively large amount of helium contained in it, 1 gram of the mineral gave off 9 cc. of helium gas.

The newly discovered element was obtained from the mineral as follows: The mineral was fused with sodium disulphate and the residue, insoluble in water, was treated with dilute, boiling hydrochloric acid. The insoluble sulphates were

[1] J. Chim. Phys., 3, 617 (1905).

then fused with sodium carbonate. The barium carbonate thus obtained contained the radioactive matter in the mineral. The radium was separated by fractional crystallization of the bromides; the bromide of the new element was found to be more soluble than barium bromide.

The new element resembles the rare earths. It forms a soluble sulphate which distinguishes it from radium. It is different from thorium in that its oxalate is insoluble in an excess of ammonium oxalate.

The new substance gives off an emanation that is identical with the thorium emanation. This is shown by its rate of decay and by the rate at which the excited activity produced by it decays.

The radioactivity of radiothorium, measured by the amount of the emanation obtainable from a given quantity of it, is *five hundred thousand times that of thorium.*

Ramsay gives the following summary of the results obtained with radiothorium: Radiothorium gives off the same emanation as thorium, but in incomparably larger quantity. The conclusion is drawn that thorium probably contains a trace of radiothorium, to which it owes its radioactivity. Ramsay has already succeeded in separating a part of the radioactivity from thorium by adding a salt of barium and then sulphuric acid. A part of the radiothorium is thus precipitated along with the barium.

Ramsay suggests the following scheme as expressing the relation between thorium, radiothorium and the helium that occurs in thorianite:

Inactive thorium ↦ radiothorium ↦ thorium X ↦ emanation ↦ thorium A ↦ thorium B ↦ ? ↦ helium.

Thus, the helium found in thorianite is formed from radiothorium. H. C. J.

REVIEWS.

REFLECTIONS SUGGESTED BY THE NEW THEORY OF MATTER. Being the Presidential Address before the British Association for the Advancement of Science, Cambridge, August 17, 1904. By the RIGHT HON. ARTHUR JAMES BALFOUR, M.P. London, New York and Bombay: Longmans, Green & Co. 1904. pp. 24. Price, 1 Shilling net.

As would be inferred from the title, the address deals with the new views pertaining to the nature of matter, that have had their origin especially in the Cavendish laboratory. The coordination of our knowledge and the unifying effect upon

physical and chemical science, resulting from the electrical conception of the nature of all matter, are pointed out.

The address is admirably written and well worthy of study on the part of all men of science, whatever their special sphere.

H. C. J.

ELETTRICITA E MATERIA. del DR. J. J. THOMSON, Professore di Fisica sperimentale nell' Università di Cambridge Membro della Societa Reale di Londra, ecc. Traduzione con Aggunte del DR. G. FAE, Libero Docente in Fisica sperimentale Professore nel R. LICEO PARINI di Milano, con 18 incisioni. Milano: Ulrico Hoepli, Editore Libraio della Real Casa. 1905. pp. 191.

Professor Thomson's Yale lectures have already been translated into German. The Italian translation has now appeared. It serves to show how widely the views of Thomson, on the relation between matter and electricity, have been accepted. The future will probably look upon these generalizations as nothing less than epoch-making in character. It is not every important advance in science that receives such wide support so quickly after it is made.

H. C. J.

DIE WISSENSCHAFT. Sammlung Naturwissenschaftlicher und Mathematischer Monographien.

DIE PHYSIKALISCHEN EIGENSCHAFTEN DER SEEN. By DR. OTTO FREIHERR, von und zu AUFSESS, Assistant für Physik an der Königl. Technischen Hochschule München. Braunschweig: Druck und Verlag von Friedrich Viewig und Sohn. 1905. pp. 120. Price, M. 3.

This little book, which is illustrated by 36 diagrams, is not intended for the professional limnologist but for those who, having some slight general scientific knowledge, desire to obtain an intelligent appreciation of the physical properties of lakes and to become acquainted with the methods which are in use, at present, for the collection of the data on which this knowledge is based. After the introductory portion, pp. x + 5, the remainder of the book is divided into four parts dealing, respectively, with "mechanics," pp. 28; acoustics, pp. 3; optics, pp. 53; thermal properties, pp. 31. At the end is given a list of more special and advanced works, which will be found useful to any who desire to study the subject in greater detail. The general style of the book is clear and pleasant.

J. B. T.

NATURKONSTANTEN IN ALPHABETISCHER ANORDNUNG. Hilfsbuch für chemische und physikalische Rechnungen, mit Unterstützung des Internationalen Atomgewichtsausschusses. Herausgegeben von PROFESSOR DR. H. ERDMANN, Vorsteher des anorganisch-chemischen Laboratoriums der Königlichen Technischen Hochschule zu Berlin, und DR. P. KÖTHNER, Privatdocent in the same institution. Berlin: Verlag von Julius Springer. 1905. pp. 192 Price, M. 6.

This is a conveniently arranged table of many of the more

frequently used constants, such as atomic weights, melting-points, boiling-points, densities, hardness, gas constants, electrochemical constants, critical constants, etc. The volume also contains a table of fifth-place logarithms and a comparatively large amount of valuable physical-chemical data, both thermochemical and electrochemical.

The book will be very useful in any physical or chemical laboratory. H. C. J.

OUTLINES OF INORGANIC CHEMISTRY. By FRANK AUSTIN GOOCH, Professor of Chemistry in Yale University, and CLAUDE FREDERIC WALKER, Teacher of Chemistry in the High School of Commerce of New York City. New York: Macmillan & Co. 1905. Price, $1.75 net.

In this substantial work of 516 pages the authors offer something differing in many respects from most other text-books. For this reason a review as full as the merits of the book deserve would require much space. Perhaps the briefest statement of its aims may be given by quoting the preface.

"Part I. takes up the consecutive experimental development of the principles upon which systematic chemistry rests. The consideration of identity of substances, chemical change, the chemical elements, the laws of combination and chemical equivalents naturally comes first. Electrical phenomena and ions,—the ions of Faraday—the constitution of acids, bases and salts from this ionic point of view, the conditions of action and equilibrium, and the thermal relations of chemical action are all, taken in succession, based upon the recognition of equivalents—electrical, chemical, thermal. The thermal equivalents suggest individual masses or mass-units of the elements in chemical action. Symbols are developed to express these mass-units, and the idea of valence follows. The conception of the molecule grows out of consideration of the volume occupied by the gram-equivalents of gaseous substances."

"Only in the final chapter of this part is the notion of the atom introduced, with the molecule in its relation to the atom; and here are discussed also, as matters of theory, the molecule in the light of the kinetic theory of gases, the spatial relations of van 't Hoff and of Werner, some of the phenomena of solution, the electrolytic theory of dissociation and the modern conceptions of ions."

In the first part of this book the treatment of the subject is admirable. Beginning with and reasoning from simple experiments, the student is led to laws and to matters complex. Only one criticism suggests itself on this portion of the book—that some cases are too complex for students; for example,

the following on valence and water of crystallization: "The attachment of water of crystallization in many salts may be attributed to the development of residual valences in the oxygen mass-unit of the water molecule. Thus we have reason to believe that the molecule of liquid water is to be regarded as a polymerized form of the molecule of gaseous water, and such polymerization may easily be represented if we are willing to assume quadrivalence of the oxygen mass-unit." Is not the quadrivalence of oxygen rather too disputed a question to present to a student, inasmuch as it is impossible to acquaint him, at this stage of study, with the experimental work and the line of reasoning on which those who favor this view base their opinion?

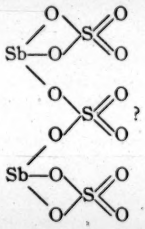
Another extract from the preface is: "In Part II. the discussion of the properties of elements and their compounds is taken up in accordance with a modification of Mendeléeff's Periodic System, which facilitates, as it seems to us, orderly treatment. Graphic symbols, explained as simply diagrammatic, are used freely. . . . . ."

While wishing to render justice to the generally full and always solid and scholarly treatment of the subject, objection may be made to the arrangement and to the excessive use of graphic symbols.

The Periodic System plays a curious part in the modern text-book. Some writers, like Ostwald and like Erdmann, relegate it to a couple of pages in the closing chapter, an extreme which must be deprecated. Others, like the present authors, make it the base of sequence in the discussion of the elements; this may be considered the other extreme. In Professor Gooch's own special modification of the periodic system, oxygen is the thirty-fourth element in sequence and has to wait its turn, yet this does not make so much difference after all, because the more important properties of oxygen were studied experimentally in the beginning of the first part of the book. As to Professor Gooch's modification of Mendeléeff, one can only say that he finds himself in good company, as it is at present quite the fashion for distinguished chemists to offer such modifications, witness Brauner, Werner and Abegg among the more recent. Whether any of these are—everything considered—an improvement on the original, is a debatable question.

As to graphic symbols—after they have been fully explained why continue to write them in full? No one does it in teaching organic chemistry; we should not find it necessary, in discussing the derivatives of triphenylmethane, to indicate the

position and valencies of each of the carbon and hydrogen atoms in the three phenyl groups. Is it really helpful to write antimony sulphate thus,



A great deal of space is occupied by such symbols which could well have been given to other things that the authors have omitted, doubtless for lack of space. As a single example, no mention is made of the hydrides or nitrides of any of the alkali or alkaline-earth metals excepting lithium, though the importance of these hydrides to the doctrine of valence toward hydrogen in the periodic system, and the importance of calcium and magnesium nitrides, as a result of absorption of nitrogen and a source of ammonia, might have secured brief mention.

The paragraphs on processes of manufacture might be profitably enlarged or modified. Thus no mention is made of the manufacture of electrolytic sodium, or of any manufacture or common use of sodium peroxide, or of any commercial method of making hydrochloric acid except as a by-product of the Leblanc soda process.

These are, however, comparatively trivial matters. Of the book as a whole, one can only express sincere approval and recommend it to the careful consideration of students and of chemists. E. R.

DIE ENTWICKELUNG DER ELEKTRISCHEN MESSUNGEN. Von DR. O. FRÖHLICH. Mit 124 eingedruckten Abbildungen. Braunschweig: Druck und verlag von Friedrich Vieweg und Sohn. 1905. pp. 192. Price, M. 6.

As the title implies, the book is largely of physical interest, dealing chiefly with the various forms of apparatus that have been used for electrical measurements. Considerable space is given to the historical development of the galvanometer, as we should expect. Similarly, the electrodynamometer is discussed at some length.

The various methods employed in electrical measurements are considered at the close of the volume. These include methods for measuring the current, electromotive force, resistance and self-induction.

The book will doubtless be useful to electrochemists, as well as physicists, in carrying out electrochemical measurements.

H. C. J.

THERMODYNAMIK TECHNISCHER GASREAKTIONEN. Sieben vorlesungen von DR. F. HABER, a. o., Professor an der Technischen Hochschule Karlsruhe i. B. Mit 19 Abbildungen. München and Berlin: Druck und verlag von R. Oldenbourg. 1905. pp. 296. Price, M. 10.

This book deals with a somewhat unusual subject. The idea of the ground covered can be gained best by a reference to the contents. It is published, as the title indicates, as a series of seven lectures, dealing especially with: The latent heat of chemical transformation and its relation to the energy of reaction; Entropy and its significance in gas reactions; Reactions that take place without change in the number of molecules; Reactions that take place with change in the number of molecules; Determination of the specific heat of gases; Determination of equilibrium in gases, etc.

The book represents an admirable piece of work, which is both of technical and scientific interest. Take the two chapters on gas reactions. It is difficult to say where a better account of the processes and conditions involved in these reactions can be found. The same remark applies to the chapter on the determination of the specific heat of gases. The book, as a whole, deserves high commendation. H. C. J.

LANDOLT-BÖRNSTEIN, PHYSIKALISCHE-CHEMISCHE TABELLEN. Dritte umgearbeitete und vermehrte Auflage. Herausgegeben von DR. RICHARD BÖRNSTEIN, Professor der Physik an der Landwirtschaftlichen Hochschule zu Berlin, und DR. WILHELM MEVERHOFFER, Professor, Privatdocent an der Universität zu Berlin. Berlin: Verlag von Julius Springer. 1905. pp. 861.

The character of the book in question is so well known as to call only for a brief notice. The present edition differs from the earlier in being much fuller, and especially in containing a large number of the physical-chemical constants that have recently been established.

The value of the book is greatly increased by references to the literature of the various subjects discussed. Unfortunately, however, in some instances, these are far from complete. This is notably the case in connection with the conductivity of aqueous solutions and the migration velocities of the ions.

This book is, of course, indispensable to all chemical libraries, especially in laboratories where research work is in progress. All working chemists must have access to their "Landolt-Börnstein." H. C. J.

A Systematic Course of Practical Organic Chemistry. By Lionel Guy Radcliffe and Frank Sturdy Sinnatt. London, New York and Bombay: Longmans, Green & Co. 1905. pp. 264.

The object of this book is to present a series of typical preparations which can be performed by a student working about 5 hours weekly, during one academic year. So far as can be judged from its perusal only, without using it in the laboratory, the authors have succeeded in this part of their task. They state in the preface that the course is intended "to induce the student to think, to read his theoretical text-books, to work intelligently and exactly and to recognize the connected character of the study of practical and theoretical organic chemistry." These are high aims; the first, at any rate, is hardly likely to be attained, owing to the unfortunate plan which has been adopted of stating the result of an experiment instead of leaving it to the student to observe it for himself. Thus, to mention one example out of many, in an experiment with benzoic acid, to show the action of heat, it is stated that "the acid ignites and burns with a smoky flame." Like the majority of English text-books, this one is burdened with a quantity of matter composed for the purpose of meeting the demands of certain examining boards, a blemish for which the authors are not to blame, because they explain that they are the victims of circumstances. The volume is not illustrated, the student being referred to model apparatus, which he is to copy for his own work. This plan is said to be advantageous. In spite of the drawbacks mentioned, the book, as a whole, makes a favorable impression and may be found useful to those teaching or studying the subject. J. B. T.

Spectroscopy. By E. C. C. Baly, F.I.C., Lecturer on Spectroscopy and Assistant Professor of Chemistry, University College, London. (Text-books of Physical Chemistry. Edited by Sir William Ramsay, K.C.B., F.R.S.) With 163 illustrations. London, New York and Bombay: Longmans, Green & Co. 1905. pp. 568. Price, $2.80.

We all welcome another of the excellent series of physical chemistries edited by Ramsay. This latest work on spectroscopy is a fit companion of such preceding volumes as Findlay's "Phase Rule" and Mellor's "Dynamics and Statics."

The work deals with spectroscopy from the time when Sir Isaac Newton, in 1666, discovered that light of different color

suffered different refraction in the same medium, up to the present.

After a historical introduction, the author takes up the prism spectroscope, discussing the separate parts—the lenses, the prism, the slit, etc., in considerable detail. The grating, and its application to spectroscopy, furnish the subject-matter for several chapters. In these the various regions of the spectra are studied at some length, including the spectra in the infra-red and in the ultra-violet.

The Zeeman effect, of course, finds its place among the newer work, and the various relations that have been pointed out between the lines produced by the same and correlated elements are developed rather fully.

The work fitly concludes with a chapter on the engine devised by Rowland for ruling the concave grating.

This book represents an admirable piece of work and is recommended to all students of the physical sciences, who must be interested in the fundamental science of spectroscopy.

H. C. J.

THE ELEMENTS OF PHYSICAL CHEMISTRY. By J. LIVINGSTON R. MORGAN, PH.D., Professor of Physical Chemistry, Columbia University. Third edition, revised and enlarged; first thousand. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1905. pp. xii + 510. Price, $3.00.

Attention has been called in this JOURNAL[1] to the first and second editions of this book. The following explanatory sentence occurs in the author's preface to the third edition.

"The ideas I have had in mind in making this revision may be summarized as follows: To bring the subject-matter up to date; to distinguish sharply between hypothesis and fact, avoiding the former as far as is possible; and to accentuate the physical meaning of the results of mathematical reasoning, *i. e.*, to employ mathematics simply as a means to an end and to make the matter as intelligible as possible, even to the non-mathematical reader."

H. S. U.

SELECT METHODS IN FOOD ANALYSIS. By HENRY LEFFMANN and WILLIAM BEAM. Second edition, revised and enlarged. Philadelphia: P. Blakiston's Son & Co. 1905. Price, $2.50.

The revision of this book shows the continued interest in works devoted to food analysis. The rapidly extending inspection of foods in the states and by the United States has created a demand for chemists who are experts in food analysis. The second edition of this book will prove of great advantage to chemists engaged in such work.

[1] THIS JOURNAL, **21**, 459; **28**, 242.

The analytic methods for the determination of physical data and of chemical data are first described. Next are considered the methods of detecting poisonous metals, colors and preservatives in foods. Following this chapter are the special methods for carbohydrates, fats and oils, dairy products, non-alcoholic beverages, condiments and spices, both fermented and distilled, and alcoholic beverages. The last chapter is devoted to the examination of flesh foods and meat extracts.

The mechanical execution of the work is very commendable. The print is plain and not too small for the ordinary reader.

Among the poisonous metals which may be found in food are mentioned tin, copper, zinc and arsenic. The chapter on the detection of colors is exceptionally well written. The usual methods of detecting preservatives are described.

Many manufacturers would take exception to the statement that ale is made from a light-colored malt, usually with the addition of glucose. The occasional presence of copper, zinc, lead and arsenic in wine is ascribed to the use of crude glucose and aniline colors. In the case of copper it is more likely to be due to the spraying, which is practiced to prevent mildew and the ravages of insects. The use of shot made of lead for cleaning bottles is, perhaps, still too common, most high-grade manufacturers use shot made of tin for this purpose.

Full references are given to the most important authorities consulted. Due credit is also given to the methods employed by the Bureau of Chemistry of the Department of Agriculture and by the Association of Official Agricultural Chemists. These methods comprise a considerable portion of the whole work. The book will serve a useful purpose as a handy volume for analysts engaged in food analysis and inspection.

H. W. W.